

Research on the Influence of Heavy Pollution Environment on Hydrophobic Substances in Silicone Rubber Materials

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Abstract: Power load forecasting is very important for power dispatching. Accurate load forecasting is of great significance for saving energy, reducing generating costs, and improving social and economic benefits. In order to accurately predict the power load, based on BP neural network theory, combined with the advantages of Clementine in dealing with big data and preventing overfitting, a neural network prediction model for large data is constructed.

Keywords: Silicone Rubber Material, Hydrophobic Substances, TGA, DSC.

1. Introduction

In recent years, with the widespread use of composite insulators, their performance in polluted environments has garnered increasing attention [1-3]. During operation, loaded insulators are exposed to various environmental factors [4-6] such as sunlight, pollution, frost, humidity, and temperature fluctuations, while also facing challenges from strong electric fields and lightning. These conditions may affect their water resistance, further accelerating their aging process. Moreover, considering that the surface electric field of composite insulators is not uniformly distributed, especially in certain specific areas, there may be phenomena of flashover instability [7]. To delve deeper into these mechanisms, this study selected high-temperature vulcanized silicone rubber samples for experimental analysis under different conditions, aiming to uncover the influencing mechanisms of their hydrophobic properties.

2. Detailed Experimentation and Associated Process

2.1. Experimental Samples and Methods

For this study, high-temperature vulcanized silicone rubber samples from the same manufacturer and batch were selected. Each sample had dimensions of 30cm×15cm×0.3cm, with a surface area of 450cm². The sample surface was smooth with uniform thickness. 6 experimental conditions were set, including deionized water soaking, low-temperature icing, and low-temperature dust+salt treatments. Long-term hydrophobicity migration tests were conducted under each condition. Based on the test results, the experimental duration was determined, with the longest being 1800h. Extractions, Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis, differential scanning calorimetry,

water spray classification, and scanning electron microscopy tests were performed. This was to ascertain the mechanism by which polluted environments influence the hydrophobic substances inside silicone rubber and subsequently establish their migration model.

2.1.1. Experimental Samples and Methods

To study the influence mechanism of polluted environments on the hydrophobic substances of silicone rubber, its chemical composition was first obtained. The silicone rubber material is a mixture formed by vulcanizing various substances like base rubber, reinforcing agents, coloring agents, strengthening agents, and vulcanizing agents at high temperatures. The primary organic substance inside is base rubber-poly(methylvinylsiloxane), which is vulcanized at high temperatures. Due to uneven cross-linking and molecular pyrolysis reactions of silicone rubber, both cross-linked macromolecules and oligomers (compounds) exist within the finished silicone rubber material. Silicone rubber molecules contain both the inorganic Si-O bond and the organic Si-CH₃ bond. The Si-CH₃ bond is the basis for its hydrophobicity. Based on current oligomer theory, oligomers (compounds) are the primary basis for the hydrophobic migration ability of silicone rubber. Two experimental schemes were set to extract substances from silicone rubber using dichloromethane as the solvent, which strongly dissolves low molecular weight polymers and doesn't dissolve inorganics or cross-linked high molecular weight polymers. The extraction process was carried out at room temperature.

Experimental Scheme 1: Silicone rubber surface material from the high-temperature test samples was soaked in dichloromethane for more than 240 hours at room temperature. After filtering out insoluble substances (cross-linked silicone rubber and inorganic fillers), the clear filtrate was heated in a water bath to remove the dichloromethane, and then evaporated until no dichloromethane remained.

Experimental Scheme 2: Diatomaceous earth from room temperature dust-covered samples were eluted with dichloromethane, soaked for more than 96 hours, and then filtered to remove the diatomaceous earth. The clear filtrate was heated in a water bath to remove the dichloromethane, and then evaporated until no dichloromethane remained.

The fresh samples contained 2.215% migratory substances, appearing as a light-yellow oily liquid. After aging at 120°C for 528h and 1656h, the extracted migratory substances from the surface and core layers were 2.141%, 2.139%, 0.312%, and 0.303%, respectively. Factory samples of the same size and weight covered with diatomaceous earth of the same concentration for 240h, 454h, and 1440h showed extracted migratory substance contents of 0.181%, 0.181%, and

0.180%, respectively.

To further verify the chemical composition of the hydrophobic substances, FTIR analysis was conducted. The following figure a-d displays the infrared spectra of small molecule compounds extracted from the surface material of fresh silicone rubber, diatomaceous earth adsorbed at room temperature for 1440h, and samples after high-temperature testing for 1656h.

BP neural network is a multi-layer network with error reverse propagation, which is composed of input layer nodes, hidden layer nodes, and output layer nodes. This process has been reduced to an acceptable level of error to the network output, or to a predetermined number of learning times. The network structure is shown in Figure 1.

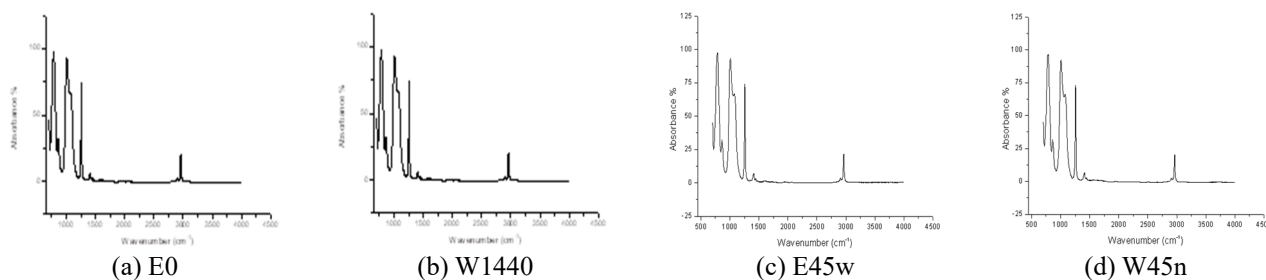


Figure 1. FTIR Spectra Analysis of Extracted Small Molecule Compounds from Silicone Rubber under Various Conditions.

The infrared spectra of the extracted low-molecular-weight substances were essentially identical, with main characteristic absorption peaks at 2905cm⁻¹ and 2962 cm⁻¹ for carbon-hydrogen bonds (C-H), 1257 cm⁻¹ and 1411cm⁻¹ for in-plane and out-of-plane bending vibrations of silicone methyl (Si-CH₃), 1010 cm⁻¹ and 1080 cm⁻¹ for stretching vibrations of siloxane bonds (Si-O-Si), and 800cm⁻¹ for stretching vibrations of silicon-carbon bonds (Si-C) and in-plane rocking of the methyl group (CH₃). These are typical FTIR spectra for polysiloxanes. However, no absorption peaks were observed in the 3200 ~ 3600cm⁻¹ range, indicating the absence of hydroxyl groups in the substance. In light of this, the migratory substance is end-capped polydimethylsiloxane with methyl groups, which, aside from its end groups, share a consistent structure with the large molecules of silicone rubber (-OH terminated). The structural formula is shown in Figure 2.

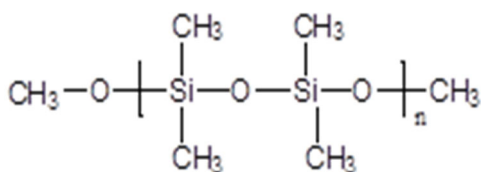


Figure 2. Small Molecular Hydrophobic Substance - Methyl-Terminated Polydimethylsiloxane

2.1.2. Study on the Variation of Hydrophobic Substances in Silicone Rubber Material under Polluted Environment

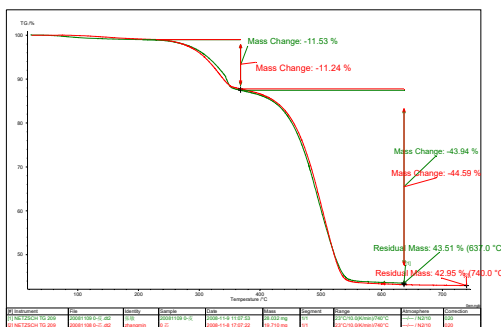
Existing theories on the migration of hydrophobic low-molecular-weight substances have provided a comprehensive

analysis and description of the migration of hydrophobic substances from the material to pollution (including air). Hence, this section primarily investigates the motion rules of hydrophobic substances within the material under the influence of pollution. Samples from different time intervals of the 6 conditions were tested using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

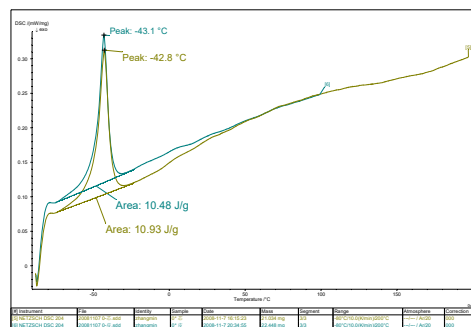
TGA, or simply TG, is a method that measures the relationship between a substance's mass and temperature or time under controlled temperature conditions. By subjecting the object to continuous temperature, its weight loss after reactions such as volatilization or decomposition at different temperatures is measured, resulting in a curve depicting its temperature and weight loss.

DSC measures the power difference (as heat) inputted into the sample and a reference material concerning temperature under controlled temperature conditions. The curve recorded by the differential scanning calorimeter is called a DSC curve, plotted with the sample's endothermic or exothermic rate, i.e., the heat flow rate dH/dt (in millijoules/second) on the y-axis, and temperature T or time t on the x-axis. It can measure various thermodynamic and kinetic parameters, such as specific heat, reaction heat, transition heat, phase diagrams, reaction rates, crystallization rates, polymer crystallinity, sample purity, etc. This method characterizes the phase changes of substances, and through the temperature range of its phase changes and its latent heat of phase transition, the type of oligomer or polymer can be identified.

(1) Fresh Silicone Rubber Material Thermal analysis tests were conducted on the surface and core layers of the silicone rubber material, with results shown in the following Figure 3.



(a) TGA Green represents the surface layer



(b) DSC Blue represents the surface layer

Figure 3. TGA and DSC Curves of the Sample

Silicone rubber material consists of base rubber, inorganic fillers (aluminum hydroxide and silica), and other substances (colorants, vulcanizing agents, structural agents, catalysts, etc.). Among these, the content of other substances is relatively minor, and the base rubber contains both low-molecular-weight hydrophobic substances and organic cross-linked macromolecules. The TGA profile indicates that the thermal weight loss curve of the silicone rubber material can be essentially divided into four stages. The first stage ranges from 220°C to 370°C. At these relatively lower temperatures, chemical bond pyrolysis in the silicone rubber macromolecules does not occur, but it can cause dehydration of aluminum hydroxide and volatilization of low-molecular-weight hydrophobic substances. The second stage ranges from 370°C to 740°C. As the temperature increases, chemical bonds like C-C, Si-O, and Si-C in the silicone rubber macromolecules break, producing volatile substances. Given that the melting points of both silica and aluminum hydroxide

exceed 1500°C, there's insufficient temperature to cause their mass loss. Hence, this stage is determined to be the decomposition and weight loss interval for the high molecular weight substances. When the temperature exceeds 740°C, only inorganic residues (like silica and alumina) remain. TGA-FTIR tests further confirmed the reactions of the aforementioned three temperature intervals. During the TGA tests at 360°C and 480°C, siloxane organic substances were detectable. Concurrently, at 380°C (FTIR test results have a certain lag), the content of -OH peaked. As all samples used in this section's 6 conditions come from the same manufacturer and batch, their formulas are consistent, and the aluminum hydroxide content is almost identical. Therefore, the weight loss in the first stage of the TGA curve can qualitatively represent the weight loss of low-molecular-weight hydrophobic substances. The FTIR test results of TGA experimental products in different temperature ranges are shown in Figure 4.

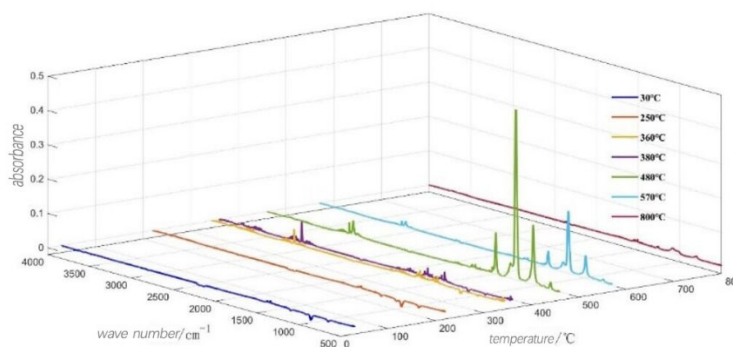


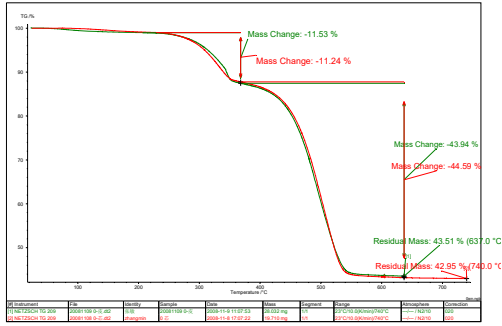
Figure 4. FTIR test results of products from the TGA experiments at different temperature ranges

The ash residue of the silicone rubber material's surface and core layers were 43.51% (at 637°C) and 42.95% (at 740°C), respectively. The content of low-molecular-weight hydrophobic substances for each was 11.53% and 11.24%, respectively, vaporizing or decomposing between 220°C and 370°C. The content of substances beginning to decompose at 370°C was 43.94% and 44.59% for each, respectively. The phase transition points of the low-molecular-weight hydrophobic substances were -43.1°C and -42.8°C, respectively. At these phase transition points, the heat changes

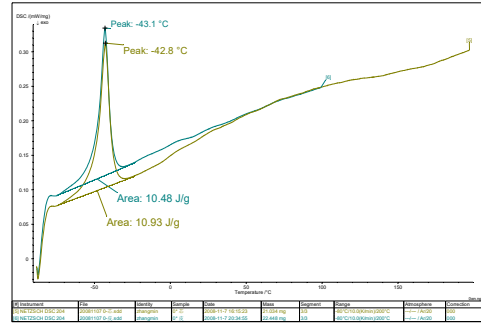
were 10.48J/g and 10.93J/g, respectively. The sharpness of this peak indicates that the composition of the silicone rubber material's surface and core layers is essentially the same.

Subsequently, this article will use deionized water as an example to demonstrate the experimental process and results.

After soaking in deionized water for 360 hours, the surface moisture was removed, and thermogravimetric analysis was conducted, as shown in the following Figure 5 (a) and (b) (red line for the surface layer and green line for the core layer).



(a) Before the experiment



(b) After immersion in deionized water for 360h

Figure 5. TGA Curves After Immersion in Deionized Water

It can be observed that after soaking in water for 360 hours, the concentration of low-molecular-weight hydrophobic substances in the silicone rubber material's surface layer decreased to 11.36%. The concentration of cross-linked silicone rubber macromolecules dropped to 42.91%, while the concentration of inorganic compounds increased to 44.38%. The concentration of hydrophobic substances in the surface layer shifted from being higher than that in the core layer to being lower. The reason for this can be analyzed as follows: Prolonged immersion in deionized water causes a slight migration of hydrophobic substances from the silicone material to the water. Organic molecules undergo intense

hydrolysis, leading to a decrease in their concentration. However, the -OH groups formed after hydrolysis have high reactivity, and they easily undergo condensation, reforming into long molecular chains, which suppresses the migration of hydrophobic substances from the inner layer to the surface.

To verify the accuracy of the above analysis, hydrophobicity, microstructure, and FTIR tests were conducted on the samples. The results are shown in Figures 6-8. To prevent the influence of deionized water during the soaking process on test results, the hydrophobicity test adopted a method of first drying followed by a secondary water spray measurement.

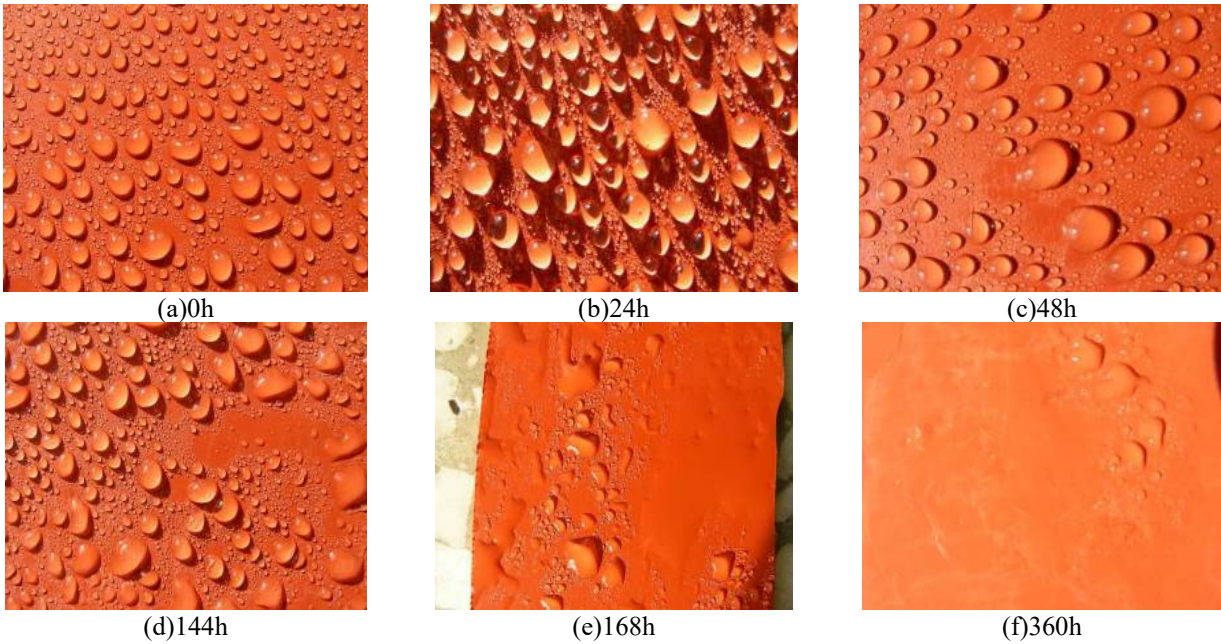


Figure 6. Surface hydrophobicity variation after immersion in deionized water

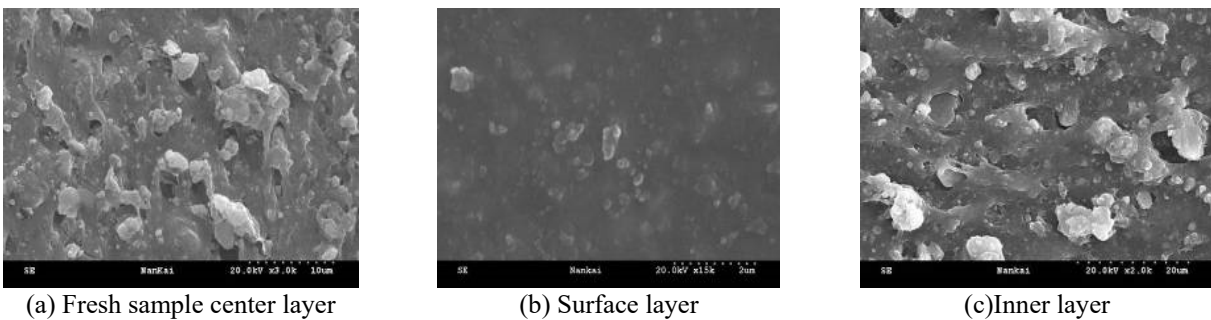


Figure 7. Microscopic Morphology of the Sample

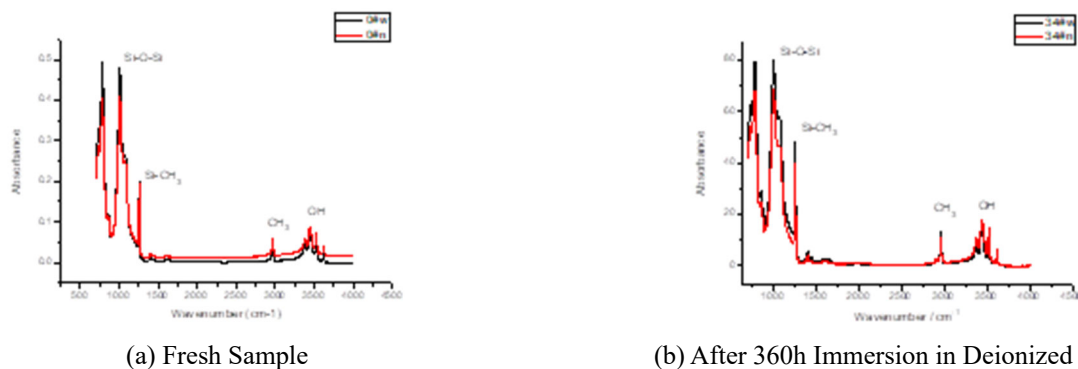


Figure 8. FTIR Spectra of the Sample

It is evident that after soaking in deionized water for 168 hours, the hydrophobic performance of the silicone rubber material's surface deteriorates significantly, and by 360 hours, it is completely lost. The amount of chunk-like substances in both the surface and inner layers increases, indicating a decrease in organic components and precipitation of inorganic fillers. The FTIR test results characterize the functional group content of organic components in the silicone rubber material, showing an increased content of -OH groups. The results consistently indicate that after long-term immersion in water, the amount of hydrophobic substances in the silicone rubber material decreases, exhibiting signs of hydrolysis. As the organic components reduce, inorganic components precipitate, increasing the material's hydrophilicity and rapidly deteriorating its hydrophobic performance. Furthermore, as the -OH groups condense, they form long-chain organic macromolecules, inhibiting the migration of hydrophobic substances from the inner layer to the surface, aligning with the TGA analysis results.

Subsequently, this study carried out experiments under various conditions (heavy ash, heavy salt, temperature, moisture, icing) to explore the mechanism influencing hydrophobic migration. These experiments were verified using microstructure, FTIR, and other analysis results, leading to the establishment of the following model:

Using the core layer as the interface, the silicone rubber material can be divided into three parts: surface pollution, surface layer, and core layer, as shown in Figure 9. The blue region represents the pollution layer, the red signifies the core layer of the silicone rubber material, and the interface between the two is the silicone rubber material surface layer (green). The pollution layer represents elements like air, moisture, icing, ash, and salt.

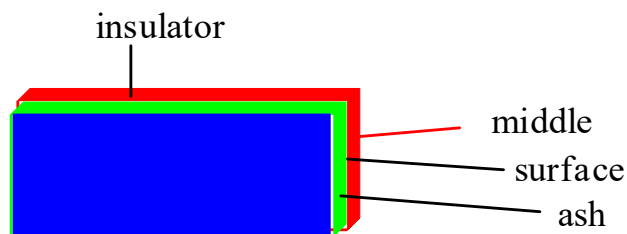


Figure 9. Schematic of Silicone Rubber Material with Contamination Layer

Hydrophobic substances (low molecular weight methyl-terminated polysiloxanes) exist in equilibrium between the inner layer, surface layer, and pollution layer of the silicone rubber material: When the surface of the silicone rubber

material is contaminated (pollutants include air, ash, salt, ash + salt, moisture, ice, etc.), hydrophobic substances from the material's surface layer migrate to the pollution layer, while those from the material's core layer migrate to the surface layer. Due to the adsorptive action of pollutants on hydrophobic substances, a relatively high concentration of these substances is maintained in the material's surface layer. Over time, the concentration of hydrophobic substances in the pollutants closest to the material continually rises, possibly even reaching saturation, and then migrates further away. Still, the migration speed decreases. At this point, the migration of hydrophobic substances from the material's core and surface layers can only compensate for the loss due to migration to more distant pollutants. The movement of hydrophobic substances reaches equilibrium between the material's core layer, surface layer, and pollution layer. The migration of hydrophobicity is related to the type of pollutant, temperature, and concentration of hydrophobic substances and is overall a process influenced by migration pathways.

During this migration, when the pollutant layer on the silicone rubber material's surface consists of water, salt, and icing that suppress hydrophobic migration, the hydrophobic substances gradually hydrolyze. The migration of hydrophobic substances from the core layer to the surface layer is restricted, leading to an accumulation of hydrophobic substances in the core layer. The content of hydrophobic substances in the surface layer decreases due to hydrolysis and insufficient replenishment. When the pollution layer contains ash, the strong adsorption by the ash causes hydrophobic substances to migrate from the material's surface layer to the pollutants. The migration speed of hydrophobic substances from the core layer to the surface layer accelerates, and the breakdown speed of the silicone rubber macromolecules in the surface layer also increases. As a result, the concentration of hydrophobic substances in the surface layer rises relative to the core layer.

Simultaneously, when the pollution layer contains ash (in conditions like low-temperature ash coverage, room temperature ash coverage, and low-temperature ash + salt coverage), due to the adsorption action of the ash, the concentration of hydrophobic substances in the material dynamically balances, with the surface layer slightly higher than the core layer. When the pollution layer doesn't contain ash (in conditions like water immersion and low-temperature icing), due to the poor adsorptive capacity of the pollution layer, the concentration of hydrophobic substances in the material dynamically balances, with the surface layer slightly lower than the core layer. A detailed description is shown in Figure 10.

PS: I, S, W means Ice, Salt, and Water are Contaminants.

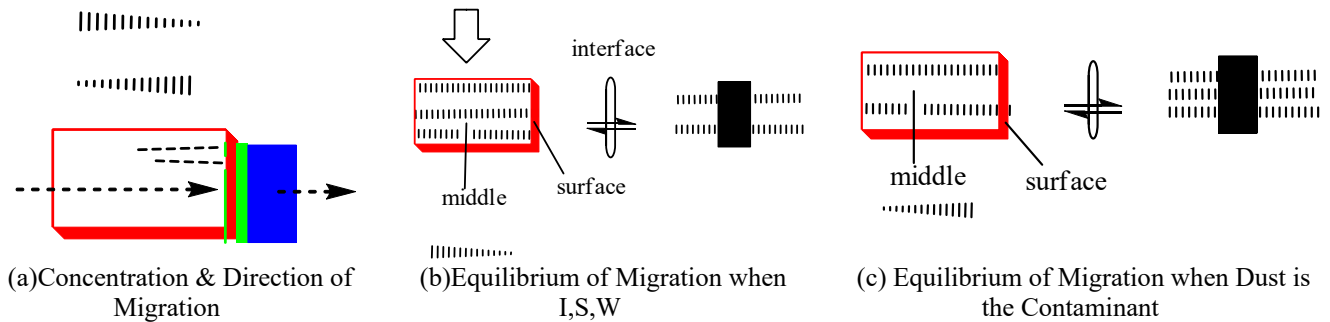


Figure 10. Hydrophobic Migration Model

3. Conclusion

Through six innovative experiments, utilizing thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) methods, this study analyzed relevant properties and arrived at the following conclusions:

1) Structure of Silicone Rubber Material: Silicone rubber material mainly comprises three distinct structural levels. First is the core layer, which serves as the heart of the material. Adjacent to the core is the surface layer, which acts as a transitional and protective segment. The outermost layer is the pollution layer, easily influenced by external conditions, and primarily accumulates components like air, moisture, ice, ash, and salts.

2) Migration of Hydrophobic Substances: In silicone rubber, hydrophobic substances do not exist statically but instead exhibit dynamic migration between different layers. This migration process is complex, and influenced by various external and internal factors. The type of pollutant, ambient temperature, and concentration of hydrophobic substances in the material can all impact its migration rate and direction.

3) Effects of Pollutants on Hydrophobic Substances: The composition of the pollution layer significantly impacts the concentration and distribution of hydrophobic substances in silicone rubber. For instance, when the pollution layer contains a higher proportion of ash, the adsorptive capacity of the ash prompts a faster migration of hydrophobic substances from the core layer to the surface layer. Conversely, when the pollution layer primarily consists of water, salts, and ice, these substances inhibit the migration of hydrophobic substances,

leading to their accumulation in the core layer and a relative decrease in the surface layer.

References

- [1] Zeng Leilei, Zhang Yu, Zeng Xin, et al. Review on the Aging State Assessment Method of Composite Insulator Silicone Rubber Skirt[J]. *Electric Porcelain & Insulator*, 2022(02): 139-145+152. DOI: 10.16188/j.isa.1003-8337.2022.02.021.
- [2] Zhang Zhong. Review of DC Flash Characteristics of Insulators[J]. *Insulating Materials*, 2017, 50(01): 8-12. DOI: 10.16790/j.cnki.1009-9239.im.2017.01.002.
- [3] Luo Mingwu, Xiao Daibo. Review on the Artificial Pollution Test Method of Composite Insulators[J]. *High Voltage Apparatus*, 2012, 48(10): 120-125. DOI: 10.13296/j.1001-1609.hva.2012.10.023.
- [4] Sun Weizhong. Impact of Temperature and Acidity-Alkalinity on Hydrophobicity of Composite Insulators[J]. *Yunnan Electric Power Technology*, 2016, 44(05): 48-51.
- [5] Jing Xingdong. Study on the Impact of Sand and Dust Environment on the Hydrophobicity of High-Speed Train Composite Insulators[D]. Southwest Jiaotong University, 2017.
- [6] Cui Wenjun, Su Huafeng, Li Junming, et al. Impact of Hydrophobicity on Flashover Voltage of Composite Insulators under Light Icing Conditions[J]. *High Voltage Engineering*, 2012, 38(10): 2617-2622.
- [7] Sha Weiyan, Luo Yan, Ma Penghuan, et al. Surface Discharge and Electric Field Characteristics of GIS Basin Insulators under Different Metal Particle Defects[J]. *Insulating Materials*, 2023, 56(09): 89-93. DOI: 10.16790/j.cnki.1009-9239.im.2023.09.016.