Research on Environmental Protection Treatment for Ex-Service SF$_6$ Adsorbent

GANG WEI$^{\dagger}$, YICHUN BAI$^{\dagger}$, MIN HU$^{\dagger}$, ZHENGQIN CAO$^{\dagger}$, AND WEI FU$^{\dagger}$

College of Electrical Engineering, Chongqing University of Science and Technology, Chongqing 401331, China

Corresponding author: Zhengqin Cao (caozhengqin@vip.sina.com)

This work was supported in part by the Chongqing Technological Innovation and Application Development Project under Grant Cstc2019jscx-msxm0182, and in part by the Research Foundation of Chongqing University of Science and Technology under Grant Ckrc2019043.

ABSTRACT SF$_6$ adsorbents absorb many toxic SF$_6$ decomposition products, such as SOF$_2$, SO$_2$F$_2$, and H$_2$S. Ex-service SF$_6$ adsorbents that did not undergo environmentally friendly processing will seriously harm the environment. In this work, thermogravimetric analysis and Fourier transform infrared spectroscopy were used to investigate the adsorbates of ex-service SF$_6$ adsorbents. Adsorbent recycling based on the thermal method was also studied. The vacuum thermal method increased the recycling efficiency of ex-service SF$_6$ adsorbents to 85%–90%. In addition, the adsorbents recovered through thermal method could be reused in SF$_6$-gas-insulated equipment. Considering their influence on equipment operation and maintenance, a harmless treatment technology for ex-service SF$_6$ adsorbents with Ca(OH)$_2$ was proposed. The adsorption and desorption behaviors of SF$_6$ adsorbents were predicted via destiny functional theory. The best treatment effect could be obtained when the Ca(OH)$_2$ amount was equal to 20% of the treatment weight of the adsorbents, and the treatment temperature was maintained at 90 °C. The economic feasibility of the harmless treatment for ex-service SF$_6$ adsorbents with Ca(OH)$_2$ was higher than that of the thermal method.

INDEX TERMS SF$_6$ adsorbent, Fourier transform infrared spectroscopy, harmless treatment.

I. INTRODUCTION

SF$_6$-gas-insulated equipment is extensively applied in power electrical systems because of its high reliability, compact construction, and small land occupation [1]–[5]. However, under partial discharge (PD), SF$_6$ gas generates SOF$_2$, SO$_2$F$_2$, H$_2$S, and other toxic substances with a small amount of impurity gases, such as moisture and oxygen [6]–[9], which corrode and reduce the insulation of gas-insulated equipment [10]. To eliminate this effect, using special adsorbent to absorb moisture and various toxic SF$_6$ decomposition products in the gas chambers of SF$_6$-insulated equipment can maintain the dryness and purity of SF$_6$ and ensure the insulation strength of SF$_6$ [11], [12]. Studies on special adsorbent for SF$_6$-insulated-equipment are mainly focused on the adsorption and influence of adsorbent on SF$_6$ decomposition component gases under PD [13]–[17]. However, the service life of early SF$_6$-insulated instruments have exceeded 20 years, and most of them have entered their maintenance periods or directly facing retirement. Hence, large amounts of SF$_6$ adsorbent will be discarded. Since the SF$_6$ adsorbent will adsorb a large amount of toxic products decomposed by SF6 during service, it will greatly harm the environment when not subjected to environmentally friendly processing. Therefore, research on the recycling and environmentally friendly treatment of special adsorbent for SF$_6$ insulation equipment is important for environmental protection.

In view of this urgent problem, this work analyzed the toxic components of ex-service SF$_6$ adsorbent. Several treatment technologies for special adsorbent for SF$_6$-insulated equipment were studied and compared, and the best processing method was proposed.

II. ANALYSIS OF THE ADSORPTION COMPONENTS OF EX-SERVICE SF$_6$ ADSORBENTS

A. EXPERIMENTAL OBJECT

SF$_6$ adsorbent are widely applied in SF$_6$-insulated equipment (e.g., SF$_6$ insulated circuits, SF$_6$ insulated breakers, SF$_6$-insulated CTs, and SF$_6$-insulated composite apparatus) to remove moisture and various toxic SF$_6$ decomposition products, such as SF$_4$, SOF$_2$, H$_2$S, HF, and other low-fluorine sulfides. In this work, the most widely used ex-service...
KDHF-03 molecular sieve adsorbent (chemical formula: Al$_2$O$_3$·4SiO$_2$·xFe$_2$O$_3$·yMgO·nH$_2$O) was chosen as the test sample. Adsorption components of KDHF-03 molecular sieve adsorbent were analyzed by using Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) to guide the environmentally friendly treatment of the ex-service SF$_6$ adsorbent.

**B. EXPERIMENTAL PROCEDURES**

The chemical components of the ex-service KDHF-03 molecular sieve adsorbent was analyzed with a FTIR meter. The decomposition gas types of the adsorbent were then determined by comparing the FTIR spectra of the main components in the molecular sieve with those of SF$_6$ decomposition gas. In addition, the temperature of the thermal desorption of the ex-service KDHF-03 molecular sieve adsorbent was obtained with a thermogravimetric analyzer, and thermogravimetric curves were acquired to determine the desorption temperature of an adsorbate in the adsorbent.

1) **FTIR ANALYSIS**

1) Samples were ground for 10 min by using a ball mill.
2) A small amount of powder was weighed with a balance. The powder was mixed with dried KBr and then preformed into a window sheet for FTIR analysis.
3) The window sheet was placed on the FTIR meter to analyze chemical groups on the adsorbent surface. The FTIR time-domain spectrum of the sample was acquired.
4) The frequency–domain spectrum, wherein the wave number was taken as the function, that is, the infrared spectrum, was obtained through fast Fourier transform.
5) The data were recorded, and the experimental instruments were tidied up.

2) **TGA EXPERIMENT**

1) The balance was used to take a small amount of an evenly ground sample.
2) The sample was placed in the crucible of the thermogravimetric analysis instrument.
3) The crucible was placed in the thermogravimetric analysis instrument, heated with nitrogen, and allowed to stand for 3 h.
4) The heating speed program was set to 5 °C/min, and the termination temperature was set to 600 °C. The measurement was started.
5) The thermogravimetric curve was obtained at the end of the measurement.
6) The data were recorded, and the experimental instruments were tidied up.

**C. RESULTS AND ANALYSIS**

The FTIR spectrum of the ex-service KDHF-03 molecular sieve adsorbent is shown in Fig.1. Absorption peaks were seen at 3500, 1380, 1000, 758, 680, 569, 460, and 448 cm$^{-1}$. These absorption peaks were identified as the absorption peaks of SF$_4$, H$_2$O, Al$_2$O$_3$, SOF$_2$, SO$_2$, SOF$_4$, SO$_2$F$_2$, HF, and SiO$_2$ by comparing the infrared spectrum absorption wave data of the main components in the molecular sieve and the main decomposition products of SF$_6$ gas. H$_2$O originated from the surface of a part of the equipment; SiO$_2$ and Al$_2$O$_3$ were derived from the absorbent; SF$_4$ was produced by the decomposition of SF$_6$ molecules under PD or overheating; and SOF$_2$, SO$_2$, SOF$_4$, SO$_2$F$_2$, and HF were generated by a series of chemical reactions among the primary SF$_6$ decomposition products with H$_2$O, O$_2$, or metal vapor in the equipment [18]–[20]. Therefore, the main substances adsorbed by KDHF-03 molecular sieve adsorbent were H$_2$O, SOF$_2$, SO$_2$, SO$_2$F$_2$, SOF$_4$, SF$_4$, and HF.

As shown in Fig.2, the TG curve of KDHF-03 molecular sieve adsorbent powder reflected the weight of the thermally processed KDHF-03 molecular sieve adsorbent as a function of temperature change. As displayed in the graph, the weight loss of KDHF-03 molecular sieve adsorbent gradually accelerated during thermal processing at room temperature to approximately 120 °C. In agreement with the FTIR spectrum of the adsorbent, the highest water content in the adsorbent, this result revealed that the weight loss interval was mainly caused by water desorption on the adsorbent surface and...
bound water. In addition, high weight loss indicated that water was the main adsorbate component of the SF₆ adsorbent. The TG curve of KDHF-03 molecular sieve adsorbent was gentle when the temperature ranged from 120 °C to 300 °C because of the desorption of SF₆ gas decomposition products. Moreover, the gentle weight loss curve indicates that the weight loss of the adsorbent in this temperature range was low and that the total weight loss of the adsorbed SF₆ decomposition products was small. When the temperature exceeded 300 °C, the adsorbent underwent a small weight loss stage, but its weight verged on stable. This phenomenon could be attributed to the almost complete desorption of water and SF₆ gas decomposition products from the adsorbent.

Under drying, SOF₂, SO₂, SO₂F₂, SOF₄, and SF₄ underwent simple physical adsorption onto the adsorbent (aluminum oxide). SOF₂, SO₂, SO₂F₂, SOF₄, and SF₄ combined with water to form acidic products, whereas aluminum oxide and water formed alkaline products. The acidic products reacted with the alkaline products, and the decomposition products were chemically adsorbed on the surface of the adsorbent. Therefore, the main objective of recovery treatment is to remove water, and that of the harmless treatment is to fix fluoride content.

III. RECOVERY EXPERIMENT ON SF₆ ADSORBENT

A. PRINCIPLES OF THERMAL PROCESSING

Thermal processing aims to increase the vibrational energy of adsorbate molecules by external heating, thereby changing the adsorption equilibrium and separating the adsorbate from the adsorbent or achieving the thermal decomposition of the adsorbent. Adsorption potential energy and adsorption heat are involved in thermal processing. The adsorbent molecules are electrically neutral in terms of adsorption potential energy. However, the most external atom layer of the adsorbent molecules is unrestrained by atoms with opposite charges and is electrically unbalanced, thus inducing the adsorbent molecules to capture other external molecules to maintain their neutral state. Adsorption heat refers to the thermal effect generated during adsorption. During adsorption, gas molecules transfer to the superficial layer of the solid, and molecular movement drastically decelerates, thus releasing heat. The amount of adsorption heat can be used to measure the intensity of adsorption. High adsorption heat indicates strong adsorption behavior.

B. RECOVERY AND REGENERATION EXPERIMENT ON SF₆ ADSORBENT

1) EXPERIMENT ON THE SELECTION OF THERMAL PROCESSING TEMPERATURE

The thermal processing temperature of the ex-service KDHF-03 molecular sieve adsorbent should be selected before the experiment on harmless thermal processing. The optimal thermal processing temperature of the ex-service KDHF-03 molecular sieve adsorbent was determined through the contrast experiment of the TG curve at 200 °C.

The experimental steps for the selection of the thermal processing temperature are as follows:

1) Three bags of recovered ex-service KDHF-03 molecular sieve adsorbent were separated into groups A, B, and C. Each group weighed 50 g. At the same time, a brand-new unopened adsorbent was prepared as the control group (group D with 50 g).

2) Samples were dried through preheating at 20 °C–100 °C, ground, and then filtered by using a sieve with 300–500 mesh numbers.

3) Heating was started at 100 °C at the rate of 5 °C/min, and the termination temperature was 600 °C. TGA was performed for each group of adsorbents.

4) The TGA data of each group were obtained, and the TG curves of each group were also compared.

5) Comparison conclusions were obtained, and the thermal processing temperature was selected. As can be seen from Fig. 3, all the TGA curves of groups A, B, C, and D appeared to intersect at 200 °C. The turning point occurred at this point. The weight loss rate of the four groups decreased, indicating that the adsorbent desorption was completed when the treatment temperature reached 200 °C. When the temperature was less than 200 °C, the weight loss rates of the adsorbents in groups A, B, and C were higher than those in group D, indicating that thermal processing is effective for adsorbent recovery. The weight loss ratio of the adsorbent decreased after the temperature was increased to 200 °C. The adsorbent recovery effect was not significantly improved by raising the thermal processing temperature beyond 200 °C. Consequently, 200 °C was selected as the thermal processing temperature for the adsorbent.

6) The data were recorded, and the experimental instruments were tidied up.

2) CONVENTIONAL THERMAL PROCESSING EXPERIMENT

1) The ex-service KDHF-03 molecular sieve adsorbent was placed in a high-speed vibration grinding machine.
for grinding and sieving. The mesh numbers of the sieve were maintained at 300–500.
2) The filtered sorbent was divided into 50 g/portion.
3) One portion was collected and placed in a heating box for 1 h of thermal processing at 200 °C. Analogously, thermal processing was performed for 2, 4, 8, and 12 h at 200 °C. After heating, the desorbed gases were stored in a gas cylinder and then sent out to a SF₆ recovery and treatment center for further processing.
4) The adsorbent that were processed with different times and unprocessed adsorbent were subjected to FTIR analysis.
5) The data were recorded, and the experimental instruments were tidied up.

3) PERFORMANCE RECOVERY TEST
1) Approximately 50 g of sample subjected to conventional thermal processing was placed on a tray balance scale.
2) The adsorbent sample were placed in an automatic microporous physicochemical adsorption instrument.
3) The instrument was employed, and the assessment was allowed to finish.
4) The data were recorded, and the experimental instruments were organized.

C. EXPERIMENTAL RESULTS AND ANALYSIS
The FTIR spectra of the unprocessed adsorbent, adsorbent that was thermally processed for 1 h, and adsorbent that was thermally processed for 2 h are shown in Figs.4, 5, and 6, respectively. The FTIR spectra of adsorbents that were thermally processed for >2 h were omitted because they changed negligibly compared with those of the adsorbents that were thermally processed for 2 h. The unprocessed adsorbents showed evident adsorption peaks at 758, 680, 569, 460, and 448 cm⁻¹. According to the comparison of the infrared spectral absorption wave data of the decomposition products of SF₆ gas and in consideration of the measurement error caused by peak drift in FTIR analysis, these absorption peaks were attributed to SF₆ decomposition products, such as SOF₄, SF₄, SO₂F₂, and SOF₂, which might be adsorbed on the adsorbent.

With the increase in processing time, the absorption peaks of SOF₄ and SF₄ disappeared, and the absorption peak intensity of the other decomposition products declined, indicating that the chemical bonds of the sulfide functional groups broke, and the groups were released as one gas that could be desorbed. At 2 h of thermal processing, the infrared adsorption peak intensity of the SF₆ decomposition products that were adsorbed on the adsorbent declined significantly, showing that heating could eliminate the adsorbed SF₆ decomposition products.

The FTIR spectra changed slightly after 2 h of thermal processing. This change reflected that the SF₆ decomposition products in the adsorbent could be decreased significantly through processing at 200 °C and 2 h. Hence, the optimal thermal processing time was chosen as 2 h.

The specific surface area, specific volume, and pore diameter of the recovered adsorbent were determined by applying a fully automatic microporous physicochemical adsorption instrument to evaluate adsorption capability. Figs.7–9 show the change trends of the specific surface area, specific volume, and pore diameter of the adsorbent that was recovered.
at 200 °C. In these figures, the red dotted line represents the average performance of the new unsealed adsorbent, and the green line represents the average performance of the adsorbent after conventional heat treatment. The specific surface area and specific volume showed a stable trend after 2 h of thermal processing, indicating that the adsorption performance of the adsorbent had reached saturation after 2 h of thermal processing. By contrast, the pore size increased linearly with the extension of thermal processing time and exceeded the average pore size of the new unsealed adsorbent between 2–2.5 h. This behavior indicated that the adsorbent decomposed after the thermal processing time of 2.5 h. The following conclusion for the conventional thermal processing of adsorbents was obtained through comparative analysis: The optimal heating temperature of conventional heat treatment was 200 °C. However, the recovery effect was not evident when the temperature exceeded 200 °C. The optimal heating time of conventional thermal processing was 2 h, and the adsorbent itself degraded when the thermal processing time exceeded 2 h. The conventional thermal processing method could not meet the requirements of adsorbent recovery, and its performance recovery rate was only 60%. Adsorption regeneration capacity slightly increased with the extension of thermal processing time, but this effect was not evident.

D. IMPROVEMENT OF THE THERMAL PROCESSING METHOD

Given that adsorbent recycling is based on ordinary thermal processing, its treatment efficiency is low. Therefore, to improve adsorbent recycling efficiency, the treatment method wherein the adsorbent was subjected to vacuum as the ambient pressure was improved, the thermodynamic equilibrium state of gas on the surface of the gas–solid was changed, and the desorption ability of adsorbed gas from the inner surface of adsorbent was improved.

1) PRINCIPLE OF VACUUM THERMAL PROCESSING

The adsorption potential energy and adsorption heat of adsorbents with adsorbate in a vacuum are lower than those under atmospheric pressure, thus increasing the vibration energy of the adsorbate molecules such that the pressure gradient force inside and outside the molecular sieve adsorbent is increased and the gas adsorbate inside the molecular sieve is easily removed.

2) EXPERIMENTAL STEPS

1) KDHF-03 molecular sieve adsorbent was placed in a high-speed vibration grinding machine for grinding and sieving. The mesh number of the sieve was maintained at 300–500.
2) A 10 g sample of the filtered adsorbents was collected and placed in a crucible.
3) A total of 10 g of sample was placed in a vacuum rapid cold–hot shock test box, and the heating procedure was performed at 200 °C with the heating time of 2 h. The toxic desorption gas was stored in sealed gas bottles and delivered to the SF$_6$ regeneration workshop for treatment.
4) The procedure was initiated, and vacuum thermal processing was completed.
5) The adsorbents were subjected to FTIR analysis and the performance recovery test after vacuum thermal processing.
6) The data were recorded, and the experimental instruments were tidied up.

3) EXPERIMENTAL RESULTS AND ANALYSIS
The FTIR spectrum at 2 h of vacuum thermal processing is shown in Fig. 10. The adsorbents were subjected to FTIR analysis and the performance recovery test after vacuum thermal processing. The absorption peaks at 569 and 460 cm\(^{-1}\) successively weakened with processing time, indicating that the vacuum thermal processing of molecular sieve was beneficial for the separation of adsorbed gases. After 2 h of vacuum heating, the infrared absorption peaks of SF\(_6\) decomposition products in the adsorbents had become very weak, indicating the presence of a few decomposition products.

Figs. 11–13 show the change trends of the specific surface area, specific volume, and pore diameter of the recovered adsorbents after different times of thermal processing at 200°C under vacuum. In these figures, the red dotted line represents the average performance of new unsealed adsorbent, and the green line represents the average performance of the adsorbent after vacuum heat treatment. The specific surface area and specific volume showed a stable trend after 2 h of thermal processing under vacuum, indicating that the adsorption performance of the adsorbent had reached saturation after 2 h of vacuum thermal processing. Pore size increased linearly with the thermal processing time and exceeded the average pore size of the new unopened adsorbent during 2 h to 2.5 h of processing, indicating that vacuum heating did not improve the degradation rate of the adsorbent. Therefore, 2 h remained as the best vacuum heating time. In addition, vacuum thermal processing increased the recovery efficiency for SF\(_6\) adsorbent to 85%–90%. However, whether the ex-service adsorbent can be reused for SF\(_6\)-gas-insulated equipment after vacuum thermal processing needs further evaluation.

IV. ENVIRONMENTALLY FRIENDLY PROCESSING
A. EXPERIMENTAL PRINCIPLE
Most of the SF\(_6\) decomposition products, such as SOF\(_2\), SO\(_2\)F\(_2\), and HF, that adsorb on SF\(_6\) adsorbents are toxic...
fluoride sulfide acids and are usually treated with alkali solution [21]. NaOH, KOH, and Ca(OH)$_2$ are common alkali substances. NaOH and KOH react quickly. However, NaF or KF are soluble and easily reionize to release toxic fluorine-containing ions. By contrast, Ca(OH)$_2$ can generate CaF$_2$ sediment, which is difficult to ionize and release toxic fluorine-containing ions. However, its reaction is slow. The ex-service adsorbent powder containing fluorine sulfides is mixed with water thoroughly by controlling the appropriate temperature and stirring speed to address this problem [22]. Fluorine sulfides react with Ca(OH)$_2$ to generate CaF$_2$, CaSO$_4$, or CaSO$_3$ precipitates for harmless adsorbent treatment.

**B. EXPERIMENTAL STEPS**

1) Ex-service polluted KDHF-03 molecular sieve adsorbent samples (50 g of each portion) were collected and placed in a beaker.
2) Adequate amounts of Ca(OH)$_2$ solutions (containing 5, 10, and 20 g of Ca(OH)$_2$) were added into the container with the KDHF-03 molecular sieve adsorbent samples. These materials were reacted by stirring at different temperatures (30 $^\circ$C, 60 $^\circ$C, and 90 $^\circ$C). The pH of the solution was tested every 10 min during the reaction. The reaction time was set as 1 h.
3) The KDHF-03 molecular sieve adsorbent sample and water were separated through static layering. The turbid solution of the KDHF-03 molecular sieve adsorbent sample in the lower layer was collected.
4) The turbid solution of the KDHF-03 molecular sieve adsorbent sample was dried in an electric blast drying box for 24 h, and the SF$_6$ adsorbent powder was collected. The powder was subjected to FTIR analysis.
5) The data were recorded, and the experimental instruments were tidied up.

**C. RESULTS AND ANALYSIS**

1) **EFFECTS OF Ca(OH)$_2$ CONTENT**
The FTIR results of the adsorbent powder samples with three amounts (5, 10, and 20 g) of Ca(OH)$_2$ are shown in Fig.14. The powder sample lacked a transmission peak at 3400 cm$^{-1}$, indicating the absence of the hydroxyl group in the samples. Peaks were observed at 2900 and 1450 cm$^{-1}$, indicating that CaF$_2$ was generated in the three groups and accounted for the strongest absorption peak of CaF$_2$ at 2900 cm$^{-1}$ [23]. In addition, the normalization rates of the 5, 10, and 20 g Ca(OH)$_2$ groups at 2900 cm$^{-1}$ were 63%, 76%, and 73%, respectively. Therefore, when the amount of Ca(OH)$_2$ exceeded 20% (mass fraction) of the adsorbent, increasing the amount of Ca(OH)$_2$ did not significantly improve the fluoride sulfide removal effect in the adsorbent. At the same time, considering that excessive Ca(OH)$_2$ increases salt alkalinity [24], the best amount of Ca(OH)$_2$ in the harmless treatment of SF$_6$ adsorbent was 20% of the treatment weight of the adsorbent.

2) **EFFECTS OF REACTION TIME**
Considering that the optimal amount of Ca(OH)$_2$ in the harmless treatment of SF$_6$ adsorbent was 20% of the treatment weight of the adsorbent, we only discussed the harmless treatment of samples using 10 g of Ca(OH)$_2$ and different reaction temperatures (30 $^\circ$C, 60 $^\circ$C, and 90 $^\circ$C). The FTIR results of powder samples under different reaction times are shown in Fig.15. As shown in Fig.16, the normalization rates of the 30 $^\circ$C, 60 $^\circ$C, and 90 $^\circ$C groups at 2900 cm$^{-1}$ were 54%, 81% and 91%, respectively. High temperatures within the experimental temperature range improved the effectiveness of the harmless treatment of SF$_6$ adsorbents.
TABLE 1. Nearest distances and adsorption energy of target gas molecules on γ-Al₂O₃.

| Gases   | d (Å) | Ead       |
|---------|-------|-----------|
| SOF₂    | 1.685 | -3.141    |
| SO₂F₂   | 2.809 | -0.765    |
| HF      | 0.925 | -2.436    |

V. ANALYSIS AND COMPARISON OF METHODS

Although the conventional thermal processing recovery of adsorbents has a certain effect on adsorbent recovery, its recycling rate cannot meet the expected goal and is only approximately 60%. Vacuum thermal processing has excellent adsorbent recovery and is suitable for industrial promotion with high recovery costs. However, whether recycled adsorbents affect the operation and maintenance of devices needs to be further assessed.

The harmless treatment of the SF₆ adsorbent with Ca(OH)₂ requires only the alkalinization of the ex-service adsorbent to eliminate fluoride sulfides. Moreover, the adsorbent processed through this method can be disposed of as common industrial waste. Therefore, the harmless treatment of SF₆ adsorbent with Ca(OH)₂ is easier to operate, safer, and more reliable than the thermal processing recovery method.

VI. PREDICTION OF THE ADSORPTION AND DESORPTION BEHAVIORS OF SF₆ ADSORBENTS

The adsorption and desorption properties of the decomposition gases of SF₆ on SF₆ adsorbents were investigated. The adsorption simulation was implemented in Materials Studios with the Dmol3 module based on the density functional theory. The Perdew–Burke–Ernzerhof function general gradient approximation was utilized to address electron exchange and correlation [25]. Maximum force, energy tolerance accuracy, and maximum atom displacement were selected as 0.002 Ha/Å, 1.0e⁻¹⁵ Ha, and 5 × 10⁻³ Å, respectively [26]. The k-point sample of the Monkhorst–Pack grid was sampled to 3 × 3 × 1. A smearing of 0.005 Ha was used to ensure accurate total energy results.

The simulation results for the nearest distances d (Å) and adsorption energy (Ead) of the target gas molecules on γ-Al₂O₃, which is the main adsorbate material of SF₆ adsorbent, are shown in Table 1.

The nearest distance d between the target molecule and γ-Al₂O₃ was 0.925 Å for the F close to the O atom in γ-Al₂O₃ in the HF system, 2.809 Å for the O close to the O atom in γ-Al₂O₃ in the SO₂F₂ system, and 1.685 Å for the F close to the Al atom in γ-Al₂O₃ in the SOF₂ system. The adsorption energies of HF, SO₂F₂, and SOF₂ were −2.436, −0.765, and −3.141 eV, respectively.

The decomposition gases of SF₆ could be desorbed from the surface through heating. The desorption time of the SF₆ adsorbent material (ε), that is, the time for decomposition gas desorption from the SF₆ adsorbent surface, has a relationship with potential desorption barrier and temperature as shown in formula (1) [27], [28]:

\[
\varepsilon = A^{-1}e^{(Ea/RT)}
\]

where A is the attempt frequency, 10¹² S⁻¹ [29]; R is the universal gas constant; T is the temperature (unit is K); and Ea is the potential desorption barrier of SOF₂, SO₂F₂, and HF on the SF₆ adsorbent, the value of which is assumed to Ead. The temperatures of 373 K, 573 K, and 973 K are considered the desorption property of the SF₆ adsorbent with the calculated desorption time shown in Fig.16.

SOF₂ had the best recovery time of 1.61 × 10⁴ s at 973 K because of the high barrier to its desorption. The recovery time in the SOF₂–γ-Al₂O₃ system increased rapidly with the decrease in temperature. The recovery time of the HF–γ-Al₂O₃ system was shorter than that of the SOF₂–γ-Al₂O₃ system, and the recovery time of the SOF₂–γ-Al₂O₃ system was the lowest and even reached 8.85 ns at 973 K.

VII. CONCLUSION

FTIR analysis revealed that the SF₆ adsorbents adsorbed abundant water and SF₆ decomposition products, such as H₂O, SOF₂, SO₂, SO₂F₂, SOF₄, and SF₄, in HF during their service period.

Adsorbent recycling via conventional thermal method could recover only 60% of adsorbent performance. By contrast, vacuum thermal processing could increase adsorbent performance recovery to 85%–90%. The optimal thermal treatment time and temperature of vacuum thermal processing were 2 h and 200 °C, respectively. The optimal amount of Ca(OH)₂ in the harmless treatment of absorbents was 20%
(mass fraction) of the weight of the SF₆ adsorbent, and the optimal treatment temperature was 90 °C. Compared with conventional thermal and vacuum thermal methods, the harmless Ca(OH)₂ treatment showed greater economic feasibility and was more conducive to promotion and application.

The nearest distances, adsorption energy, and desorption recovery times of the decomposition gases of SF₆, namely, SOF₂, HF, and SO₂F₂, on γ-Al₂O₃ were obtained via simulation and calculation to predict the adsorption and desorption behaviors of SF₆ adsorbents.

REFERENCES

[1] Y. Meng and F. Zha, Detection and Supervision of SF₆ for Electrical Equipment, Beijing, China: China Electric Power Press, 2009.

[2] D. J. Tedford, L. C. L. C. Campbell, and J. T. Pender, “Modern research and development in SF₆ switchgear,” IEEE Trans. Electr. Power, vol. 29, no. 10, pp. 719–723, Oct. 1983.

[3] H.-T. Wu, C.-Q. Jiao, X. Cui, X.-F. Liu, and J.-F. Ji, “Transient electromagnetic disturbance induced on the ports of intelligent component of electronic instrument transformer due to switching operations in 500 kV GIS substations,” IEEE Access, vol. 5, pp. 5104–5112, 2017.

[4] J. Tang, F. Zeng, and X. Liang, “Transient electromagnetic disturbance induced on the ports of intelligent component of electronic instrument transformer due to switching operations in 500 kV GIS substations,” Proc. Chin. Soc. Elect. Eng., vol. 33, no. 31, pp. 211–219, 2019.

[5] S. Wu, F. Zeng, J. Tang, Q. Yao, and Y. Miao, “Triangle fault diagnosis method for SF₆ gas-insulated equipment,” IEEE Trans. Power Del., vol. 34, no. 4, pp. 1470–1477, Aug. 2019.

[6] F. Zeng, S. Wu, X. Yang, Z. Wan, J. Tang, M. Zhang, and Q. Yao, “Fault diagnosis and condition division criterion of DC gas insulated equipment based on SF₆ partial discharge decomposition characteristics,” IEEE Access, vol. 7, pp. 29869–29881, 2019.

[7] Z. Su and Y. Zhao, “Experimental investigation into effects of absorptive on detection of SF₆ decomposition products in SF₆ equipment,” High Volt. App., vol. 49, no. 6, pp. 26–37, 2013.

[8] Z. Cao, J. Tang, F. Zeng, Q. Yao, and Y. Miao, “SF₆ positive DC partial discharge decomposition components under four typical insulation defects,” IET Gener. Transm. Distrib., vol. 13, no. 1, pp. 1–8, Jan. 2019.

[9] J. Tang, Z. Cao, F. Zeng, Q. Yao, Y. Miao, and N. Qiu, “Influence of metallic materials on SF₆ decomposition components under positive DC partial discharge,” Plasma Chem. Plasma Process., vol. 37, no. 6, pp. 1523–1534, Nov. 2017.

[10] Z. Qin, Y. Zeng, and W. Zhou, “Characteristics of contents ratio of SF₆ decomposed gases in point-plate electric field and influence of Absorbs,” High Volt. Eng., vol. 43, no. 9, pp. 2919–2926, 2017.

[11] J. Tang, F. Zeng, and X. Liang, “Study on the influence of adsorbent on SF₆ decomposition characteristics under partial discharge,” Proc. Chin. Soc. Elect. Eng., vol. 34, no. 3, pp. 486–494, 2014.

[12] Y. Zhao, G. Wei, and P. Zou, “Analyzing and desorption of the absorption composition contained in the ex-service adsorbent from SF₆ gas insulated electrical equipments,” Proc. Chin. Soc. Elect. Eng., vol. 35, no. 1, pp. 227–231, 2015.

[13] W. Yuanyuan, R. Jie, L. Xiaochao, J. Shengchang, L. Li, and W. Yu, “Influences of different absorbents on the detection of SF₆ gas decomposition products,” in Proc. IEEE Int. Conf. Condition Monitor. Diagnosis, Sep. 2012, pp. 470–475.

[14] G. Lu, J. Guo, and F. Sun, “Experimental study on relationship of SF₆ decomposition products and partial discharge in gas insulated switchgear,” High Volt. App., vol. 49, no. 6, pp. 10–16, 2013.

[15] Z. Su and Y. Zhao, “Experimental investigation into effects of absorptive on detection of SF₆ decomposition products in SF₆ equipment,” High Volt. App., vol. 49, no. 6, pp. 26–31, 2013.

[16] Y.S. Ji, X.L. Yan, C.Y. Wang, G. Song, H. M. Liu, X. Y. Li, P. Cheng, and Y.C. Li, “Experimental study on SF₆ decomposition products under the stress of electrical arc,” High Volt. App., vol. 6, pp. 22–25, 2013.

[17] L. Zhong, S. Ji, J. Li, Y. Wang, Y. Cui, J. Guo, and G. Ji, “Effects of adsorbent on contents and evolving law of typical SF₆ decomposition products,” J. Xi’an Jiaotong Univ., vol. 49, no. 2, pp. 86–92, 2015.

[18] H. M. Heise, R. Kurte, P. Fischer, D. Klockow, and P. R. Janissek, “Gas analysis by infrared spectroscopy as a tool for electrical fault diagnostics in SF₆ insulated equipment,” Fresenius J. Anal. Chem., vol. 358, nos. 7–8, pp. 793–799, Jul. 1997.

[19] W. Ding, R. Hayashi, K. Ochi, J. Suehiro, K. Imasaka, M. Hara, N. Sano, E. Nagao, and T. Minagawa, “Analysis of PD-generated SF₆ decomposition gases adsorbed on carbon nanotubes,” IEEE Trans. Dielectr. Electr. Insul., vol. 13, no. 6, pp. 1200–1207, Dec. 2006.

[20] I. Sauer, H. W. Ellis, and L. G. Christophorou, “Neutral decomposition products in spark breakdown of SF₆,” IEEE Trans. Electr. Insul., vol. EI-21, no. 2, pp. 111–120, Apr. 1986.

[21] J. Wang, “Decomposition gases of sulfur hexafluoride and treating methods,” Chem. Propell. Polym. Mater., vol. 1, no. 6, pp. 16–18, Jul. 2003.

[22] A. K. Coonar, S. P. Jones, and G. J. Pearson, “An ex vivo investigation into the fluoride release and absorption profiles of three orthodontic adhesives,” Eur. J. Orthodontics, vol. 23, no. 4, pp. 417–424, Aug. 2001.

[23] T. R. Yang, Adsort’s Fundamentals and Applications. Beijing, China: Higher Education Press, 2010.

[24] Y. Liu and Q. Chen, “Environmentally dissipative properties of calcium compounds (Calcium Carbonate, Calcium Oxide, Calcium Hydroxide) filled plastics and their environmental significance,” in Proc. Natl. Ca. Mater. Ind. Conf., Kunming, China Apr. 2005.

[25] Z. Cui, X. Zhang, Y. Li, D. Chen, Y. Li, and H. Xiao, “Theoretical study of SF₆ decomposition on the MoS2 monolayer doped with ag, ni, au, pt: A first-principles study,” Adsorption, vol. 25, no. 2, pp. 225–233, Feb. 2019.

[26] X. Zhang, L. Yu, J. Tie, and X. Dong, “Gas sensitivity and sensing mechanism studies on au-doped TiO2 nanotube arrays for detecting SF₆ decomposed components,” Sensors, vol. 14, no. 10, pp. 19517–19532, 2014.

[27] K. Patel, B. Roondhe, S. D. Dabhi, and P. K. Jha, “A new flatland buddy as toxic gas scavenger: A first principles study,” J. Hazardous Mater., vol. 351, pp. 337–345, Jun. 2018.

[28] Y.-H. Zhang, Y.-B. Chen, K.-G. Zhou, C.-H. Liu, J. Zeng, H.-L. Zhang, and Y. Peng, “Improving gas sensing properties of graphene by introducing dopants and defects: A first-principles study,” Nanotechnology, vol. 20, no. 18, May 2009, Art. no. 185504.

[29] S. Peng, K. Cho, P. Qi, and H. Dai, “An initial study of CNT NO2 gas sensor,” Chem. Phys. Lett., vol. 387, nos. 4–6, pp. 271–276, Apr. 2004.

GANG WEI received the Ph.D. degree from the State Key Laboratory of Power Transmission Equipment and System Security and New Technology, Chongqing University, China. His current research interests include environmental protection treatment of sulfur hexafluoride adsorbent, high-voltage electrical equipment insulation online monitoring, and fault diagnosis.

YICHUN BAI was born in Chongqing, China, in 1997. She received the bachelor’s degree in electric engineering from the Chongqing University of Science and Technology, China, where she is currently pursuing the master’s degree. Her main research interests include environmental protection treatment of sulfur hexafluoride adsorbent, high-voltage electrical equipment insulation online monitoring, and fault diagnosis.
MIN HU was born in Huanggang, Hubei, China, in 1986. She received the M.A. degree in measuring and testing technologies and instruments from Southwest Petroleum University, China. Her main research interest includes insulation monitoring of electrical equipment.

ZHENGQIN CAO received the Ph.D. degree from the State Key Laboratory of Power Transmission Equipment and System Security and New Technology, Chongqing University, China. His current research interests include high-voltage electrical equipment insulation online monitoring, fault diagnosis, and gas sensors.

WEI FU was born in Chongqing, China, in 1997. He received the B.Eng. degree in electrical engineering from the Chongqing University of Science and Technology, China, where he is currently pursuing the master’s degree with the School of Electrical Engineering. His main research interest includes environmental protection treatment of sulfur hexafluoride adsorbent.