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Research on Environmental Protection Treatment for Ex-Service SF_6 Adsorbent

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ABSTRACT SF_6 adsorbents absorb many toxic SF_6 decomposition products, such as SOF_2, SO_2F_2, and H_2S. 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_2F_2, H_2S, 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.

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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_2S, HF, and other low-fluorine sulfides. In this work, the most widely used ex-service

KDHF-03 molecular sieve adsorbent (chemical formula: $Al_2O_3 \cdot 4SiO_2 \cdot xFe_2O_3 \cdot yMgO \cdot nH_2O$) 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

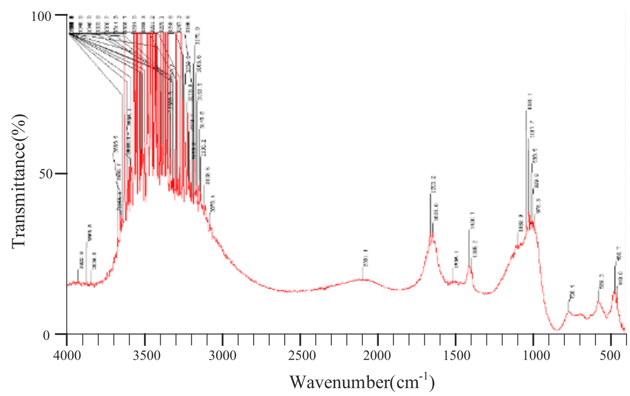


FIGURE 1. Fourier Transform Infrared (FTIR) spectrum of the ex-service KDHF-03 molecular sieve adsorbent.

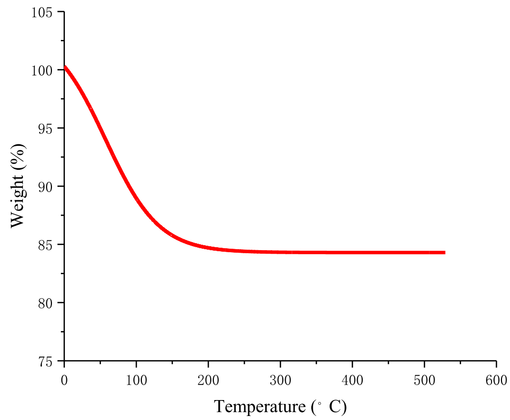


FIGURE 2. Thermal Gravimetry (TG) curve of KDHF-03 molecular sieve adsorbent powder.

peaks of SF_4, H_2O, Al_2O_3, SOF_2, SO_2, SOF_4, SO_2F_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_2O originated from the surface of a part of the equipment; SiO_2 and Al_2O_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_2F_2, and HF were generated by a series of chemical reactions among the primary SF_6 decomposition products with H_2O, O_2, or metal vapor in the equipment [18]–[20]. Therefore, the main substances adsorbed by KDHF-03 molecular sieve adsorbent were H_2O, SOF_2, SO_2, SO_2F_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 SF_6 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 SF_6 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 SF_6 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 SF_6 gas decomposition products from the adsorbent.

Under drying, SOF_2, SO_2, SO_2F_2, SOF_4, and SF_4 underwent simple physical adsorption onto the adsorbent (aluminum oxide). SOF_2, SO_2, SO_2F_2, SOF_4, and SF_4 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 SF_6 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 SF_6 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.

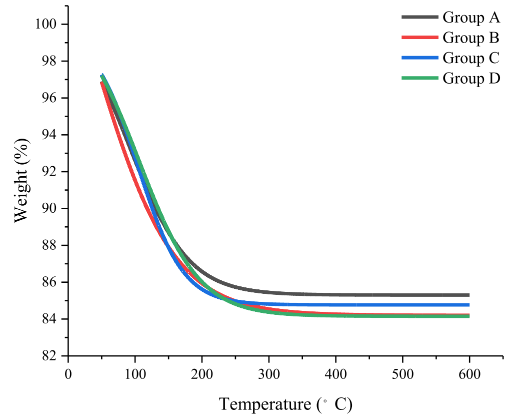


FIGURE 3. TG curves of different adsorbents.

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

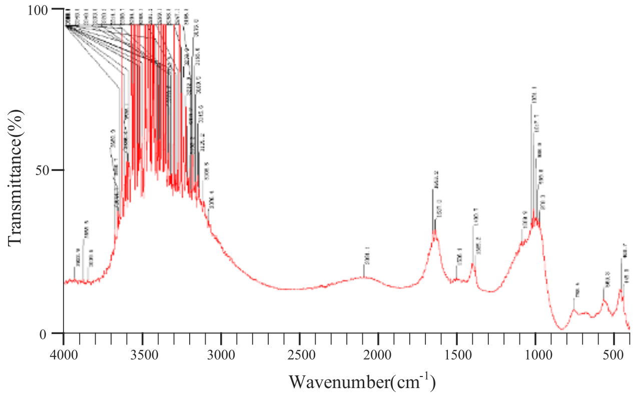


FIGURE 4. FTIR spectra of unprocessed adsorbents.

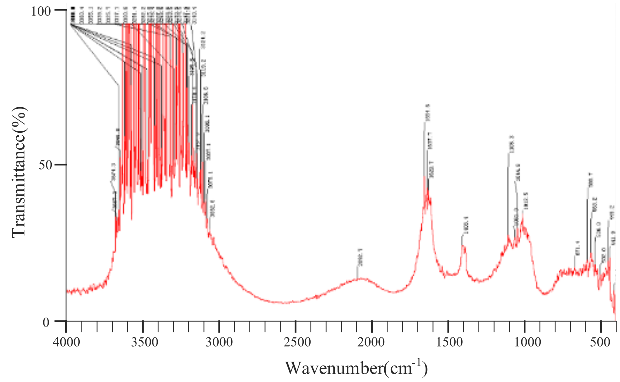


FIGURE 5. FTIR spectra of the adsorbent that was thermally processed for 1 h.

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 SF_6 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 SF_6 gas and in consideration of the measurement error caused by peak drift in FTIR analysis, these absorption peaks were attributed to SF_6 decomposition products, such as SOF_4, SF_4, SO_2F_2, and SOF_2, which might be adsorbed on the adsorbent.

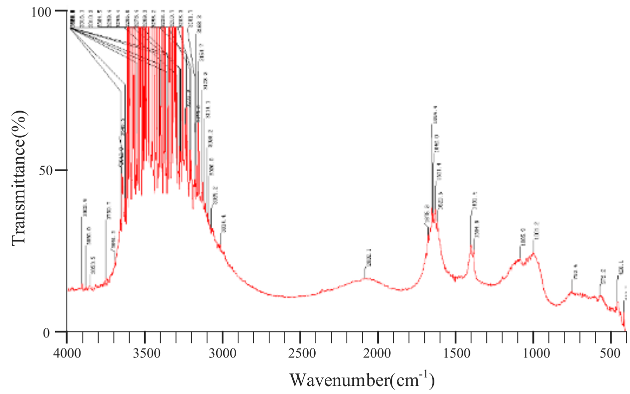


FIGURE 6. FTIR spectra of the adsorbent that was thermally processed for 2 h.

With the increase in processing time, the absorption peaks of SOF_4 and SF_4 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 SF_6 decomposition products that were adsorbed on the adsorbent declined significantly, showing that heating could eliminate the adsorbed SF_6 decomposition products.

The FTIR spectra changed slightly after 2 h of thermal processing. This change reflected that the SF_6 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

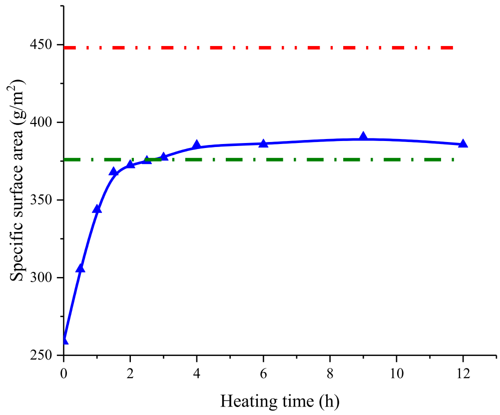


FIGURE 7. **Variation trend of the specific surface area of the adsorbent with time.**

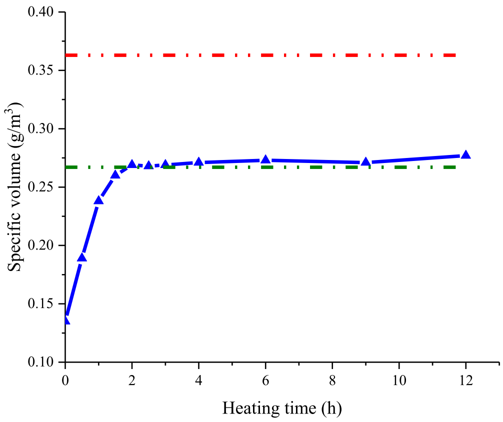


FIGURE 8. **Variation trend of the specific volume of the adsorbent with time.**

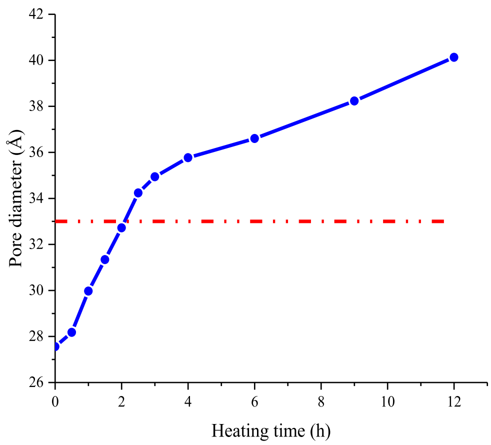


FIGURE 9. **Variation trend of the pore diameter of the adsorbent with time.**

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 ° 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.

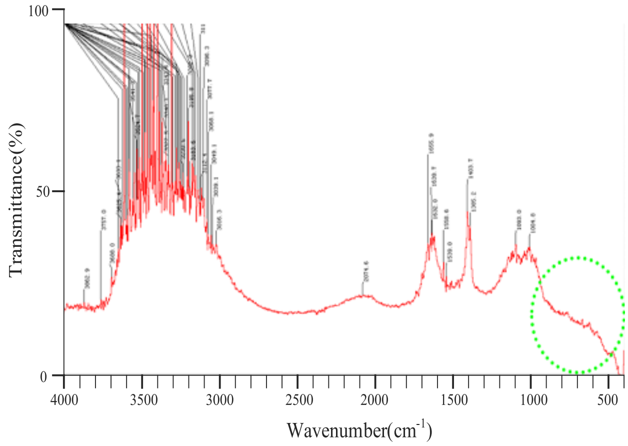


FIGURE 10. **FTIR spectrum of the adsorbent after vacuum thermal processing at 200 °C for 2 h.**

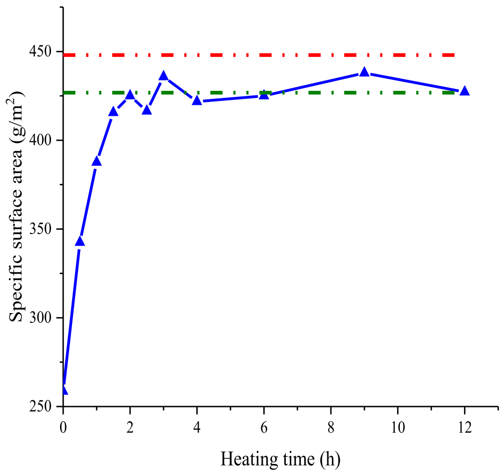


FIGURE 11. **Variation in the specific surface area of the adsorbent with time.**

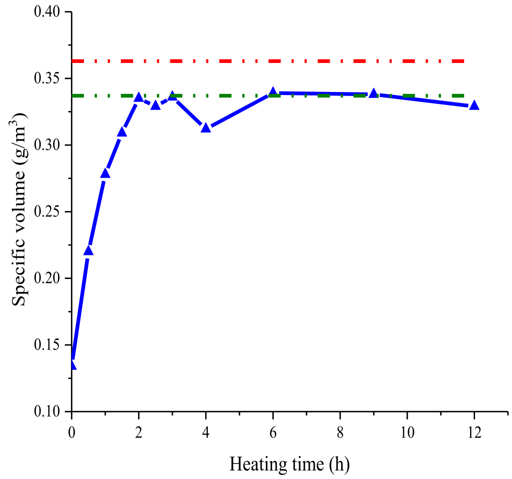


FIGURE 12. **Variation in the specific volume of the adsorbent with time.**

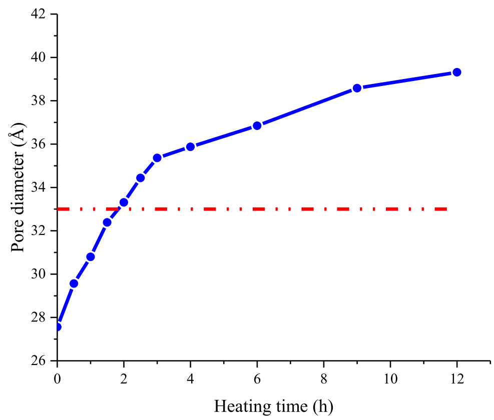


FIGURE 13. **Variation in the pore diameter of the adsorbent with time.**

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 peaks at 758 and 569 cm^{-1} disappeared after 2 h of 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_2F_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 reionized 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 CaF2, $CaSO_4$, or $CaSO_3$ precipitates for harmless adsorbent treatment.

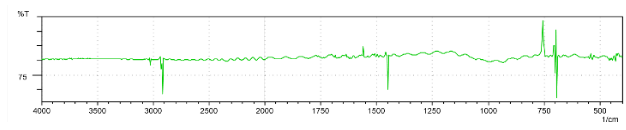
B. EXPERIMENTAL STEPS

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 °C, 60 °C, and 90 °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.

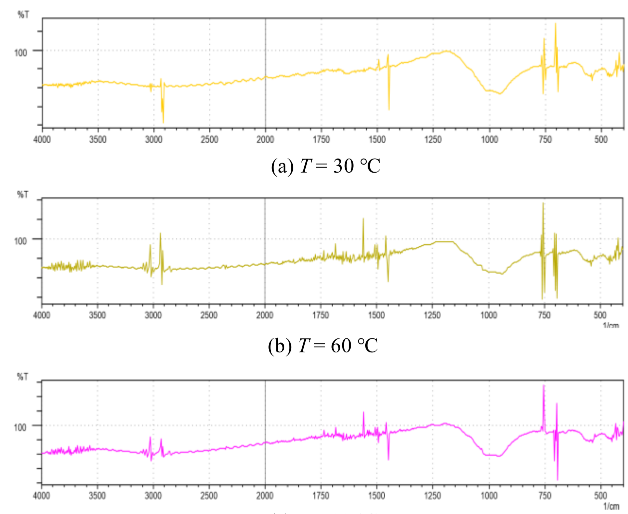


(a) $W_{Ca(OH)2} = 5$ g

(b) $W_{Ca(OH)2} = 10$ g

(c) $W_{Ca(OH)2} = 20$ g

FIGURE 14. FTIR results of powder samples with different amounts of $Ca(OH)_2$.



(a) $T = 30$ °C

(b) $T = 60$ °C

(c) $T = 90$ °C

FIGURE 15. FTIR results of powder samples with different reaction temperatures.

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 °C, 60 °C, and 90 °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 °C, 60 °C, and 90 °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-Al_2O_3.

Gases	*d* (Å)	*Ead*
SOF_2	1.685	-3.141
SO_2F_2	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 SF_6 adsorbent with $Ca(OH)_2$ requires only the alkalization 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 SF_6 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 SF_6 ADSORBENTS

The adsorption and desorption properties of the decomposition gases of SF_6 on SF_6 adsorbents were investigated. The adsorption simulation was implemented in Materials Studios with the Dmol3 module based on the density functional theory. The Perdew–Burke–Ernzerho 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^{-5} Ha, and 5×10^{-3} Å, respectively [26]. The k-point sample of the Monkhorst–Pack grid was sampled to $3 \times 3 \times 1$. 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-Al_2O_3, which is the main adsorbate material of SF_6 adsorbent, are shown in Table 1.

The nearest distance d between the target molecule and γ-Al_2O_3 was 0.925 Å for the F close to the O atom in γ-Al_2O_3 in the HF system, 2.809 Å for the O close to the O atom in γ-Al_2O_3 in the SO_2F_2 system, and 1.685 Å for the F close to the Al atom in γ-Al_2O_3 in the SOF_2 system,. The adsorption energies of HF, SO_2F_2, and SO_2F_2 were −2.436, −0.765, and −3.141 eV, respectively.

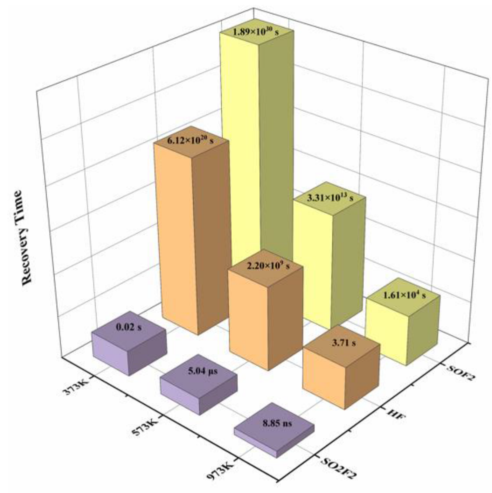


FIGURE 16. Recovery times of various target systems.

The decomposition gases of SF_6 could be desorbed from the surface through heating. The desorption time of the SF_6 adsorbent material (ε), that is, the time for decomposition gas desorption from the SF_6 adsorbent surface, has a relationship with potential desorption barrier and temperature as shown in formula (1) [27], [28]:

$$\varepsilon = A^{-1} e^{(Ea/RT)} \tag{1}$$

where A is the attempt frequency, 10^{12} S^{-1} [29]; R is the universal gas constant; T is the temperature (unit is K); and Ea is the potential desorption barrier of SOF_2, SO_2F_2, and HF on the SF_6 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 SF_6 adsorbent with the calculated desorption time shown in Fig.16.

SOF_2 had the best recovery time of 1.61×10^4 s at 973 K because of the high barrier to its desorption. The recovery time in the SOF_2–γ-Al_2O_3 system increased rapidly with the decrease in temperature. The recovery time of the HF–γ-Al_2O_3 system was shorter than that of the SOF_2–γ-Al_2O_3 system, and the recovery time of the SO_2F_2–γ-Al_2O_3 system was the lowest and even reached 8.85 ns at 973 K.

VII. CONCLUSION

FTIR analysis revealed that the SF_6 adsorbents adsorbed abundant water and SF_6 decomposition products, such as H_2O, SOF_2, SO_2, SO_2F_2, SOF_4, and SF_4, 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 SF_6 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 SF_6, namely, SOF_2, HF, and SO_2F_2, on γ-Al_2O_3 were obtained via simulation and calculation to predict the adsorption and desorption behaviors of SF_6 adsorbents.

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