Regeneration Technology of Ex-service SF$_6$ Adsorbent Using Vacuum Heat Treatment

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Abstract. Ex-service SF$_6$ adsorbent is toxic, and its direct dumping may cause environmental damages. Therefore, studying the environmental-friendly processing of ex-service SF$_6$ adsorbent has important social values. In this study, the adsorption components of the ex-service SF$_6$ adsorbent were analyzed by thermogravimetry. In order to study the most economical and effective regeneration method of SF$_6$ adsorbent, the regeneration technology of vacuum heat treatment was proposed, and the regeneration theory of vacuum heat treatment concerning adsorbent was elaborated, then followed by the experiment of vacuum heat treatment. By combining with infrared spectroscopy, the content change of harmful ingredient in adsorbent was analyzed, focused on the confirmation of vacuum heat treatment regeneration temperature, regeneration time and vacuum pressure, and the test verification on adsorption isothermal curve was performed to determine the desorption capacity of SF$_6$ molecular sieve adsorbent recycled. We found that vacuum heating can increase performance recovery rate by 85%–90%.

1. Introduction

Gas insulation equipment are increasingly used in power grids due to its small land occupation, safe operation, and low maintenance cost. Under arc or discharge, the SF$_6$ gas in operation will generate highly toxic and corrosive substances, which may affect lung, liver, kidney, and digestive functions of human bodies. Some products are corrosive and will affect equipment performance and the physical safety of operators[1-2]. With the expansion of the power system, the consumption of SF$_6$ adsorbent has gradually increased. Therefore, the processing of ex-service SF$_6$ adsorbent has important and profound significance in practical engineering and environmental protection. Currently, research on the processing of SF$_6$ adsorbent in high-voltage electrical equipment is limited.

Therefore, a recycling program for ex-service SF$_6$ adsorbent was proposed in this study. The adsorption components in the ex-service and polluted SF$_6$ adsorbent were analyzed. And then, recycling of the ex-service SF$_6$ adsorbent based on heating method was discussed.

2. Adsorption component of the SF$_6$ adsorbent

SF$_6$ adsorbent is mainly used to remove trace low fluoride, acid substances, and water, which are generated by the operation of SF$_6$ equipment and carried by the SF$_6$ gas. For the
environmental-friendly processing of the ex-service SF6 adsorbent, it is important to discuss its composition. In this study, the adsorption components of the ex-service SF$_6$ adsorbent were analyzed by thermogravimetry.

2.1 Experimental steps
Thermal decomposition temperature of the ex-service polluted SF$_6$ adsorbent was tested by thermogravimetry. The thermogravimetric (TG) curve of the adsorbent was obtained to judge the desorption temperature of substances in the adsorbent.

a. Thermogravimetric analysis (TGA)
   ① A minimum quantity of evenly grinded samples was weighed using a balance. ② Samples were placed in the crucible of the TGA instrument. ③ The crucible was placed in the TGA instrument and heated with nitrogen. It was placed on static and preheated for 3 h. ④ The temperature rising program was set at 5°C/min, and the final temperature was set at 600 °C. Next, the measurement was started. ⑤ The TG curve was gained after the measurement was finished. ⑥ Data were recorded and experimental instruments were cleaned.

b. Results and analysis

![Figure 1. TG curve of SF$_6$ adsorbent powder](image)

Figure 1. TG curve of SF$_6$ adsorbent powder

The TG curve of SF$_6$ adsorbent powder is shown in Figure 1. It reflects the mass variation of the SF$_6$ adsorbent powder with temperature in the heating process[3]. As shown in the figure, the SF$_6$ adsorbent suffers rapid weight loss in the heating process from room temperature to approximately 120°C. The weight loss is relatively high, indicating that water is the main substance adsorbed by the SF$_6$ adsorbent[4]. In the temperature interval between 120°C and 300°C, the TG curve of the SF$_6$ adsorbent is relatively stable. When the temperature exceeds 300°C, the SF$_6$ adsorbent suffers a small weight loss, and its weight tends to be stable, indicating that water and SF$_6$ degradation products are almost desorbed from the adsorbent completely.

Under drying state, SOF$_2$, SO$_2$, SO$_2$F$_2$, SOF$_4$, and SF$_4$ physically adsorb onto the adsorbent (aluminum oxide). Under wet conditions, they combine with water and form acid products, whereas the aluminum oxide reacts with water and produce alkali products. The acid and alkali products create a neutral reaction, resulting in the chemical adsorption of degradation products onto the adsorbent surface. Therefore, the key process of recycling lies in the dehydration, and that of harmless processing is the fixation of fluoride.

3. Recycling experiment

3.1 Experimental steps
a. Experiment on thermal processing temperature selection
   The best thermal processing temperature of the adsorbent is 200°C according to the contrast test of TG curves. The specific steps are as follows:
   ① Three bags of recycled polluted adsorbents were divided into groups A, B, and C. In total, 50 g of samples was collected from each group. Meanwhile, one bag of fresh closed adsorbent was prepared as the control group (group D) and was also divided into several parts (50 g/part). ② The
adsorbent samples were dried by preheating under 20°C–100°C, grinded, and then filtered with a 300–500 or higher mesh sieve. (3) Samples were heated at a constant rate of 5°C/min from 100°C to 600°C. TGA of different groups of adsorbents was performed. (4) TGA data of different groups under different processing times were acquired. The TG curves of different adsorbents were compared.

Figure 2. TG curves of different adsorbents

(5) The contrast conclusions were drawn, and the thermal processing temperature was selected. The TG curves of groups B, C, and D intersected at 200°C and showed the turning point at this point. The weight loss rate decreased, indicating that the adsorbed gas has been eliminated basically at 200°C. As shown in figure 2, when the temperature was lower than 200°C, the weight loss rates of groups A, B, and C were all higher than that of group D. This reflected that the adsorbed gases on the adsorbent had been eliminated in this temperature interval and implied that heat processing was effective for adsorbent recycling. Moreover, the weight loss rate of the adsorbent after 200°C decreased gradually, indicating that the thermal processing temperature after 200°C was insignificant to adsorbent recycling. Therefore, 200°C was selected as the thermal processing temperature of the adsorbent.

(6) Data were recorded and experimental apparatus were cleaned.

b. Conventional thermal processing experiment

(1) The ex-service polluted adsorbent was ground using a high-speed vibration grinding machine and filtered with a 300–500 or higher mesh sieve. (2) The filtered adsorbents were divided into several parts (10 g/part). (3) One part was collected and placed into a heating box. The heating temperature was set at 200°C, followed by 1 h of heat processing. The rest underwent similar process. The heating temperature was set at 200°C for 2, 4, 8, and 12 h heating process. The desorbed gases were stored in the gas bottle and sent to SF₆ recycling center for further processing. (4) Data were recorded and experimental apparatus were cleaned.

c. Performance recovery test

(1) In total, 50 g of the ex-service SF₆ adsorbent samples after conventional thermal processing was collected using a table balance. (2) The adsorbent samples were placed in a fully automated microporous physical–chemical adsorption instrument. (3) The instrument was used to obtain assessment results. (4) Data were recorded and experimental apparatus were cleaned.

3.2 Experimental results and analysis

The specific surface area, specific volume, and bore diameter of the recycling adsorbents were tested by the fully automated microporous physical–chemical adsorption instrument.[5-7]. On this basis, the adsorption ability could be evaluated. The variations of specific surface area, specific volume, and bore diameter in the performance recovery test of adsorbents under 200°C and different thermal processing times are shown in Figures 3–5 (the red dotted line is the average performance of the new unclosed adsorbent, and the green dotted line is the average performance of the adsorbent after conventional thermal processing). The specific surface area and specific volume become increasingly stable after 2 h of thermal processing, indicating that the adsorption performance reaches saturation basically at 2 h of thermal processing. However, the bore diameter presents a linear growth with the increase of thermal processing time. The bore diameter of processed adsorbents exceeds the average
bore diameter of the unprocessed absorbent at 2–2.5 h, indicating that the adsorbent will be decomposed after 2.5 h of thermal processing of the adsorbent.

It gets conclusions of the conventional thermal processing of adsorbents from the contrast analysis. The optimal temperature of the conventional thermal processing is 200°C, and excessive temperature may lead to poor recycling performance. The optimal heating time of the conventional thermal processing is 2 h; increasing the thermal processing time above 2 h may cause degradation of the adsorbent. The conventional thermal processing fails to meet the requirements of adsorbent recycling, which only claims approximately 60% of performance recovery. As the thermal processing continues, the absorption regeneration ability is slightly improved.

Figure 3. Variation trend of specific surface area of the adsorbent

Figure 4. Variation trend of specific volume of the adsorbent

Figure 5. Variation trend of bore diameter of the adsorbent

4. Improvement of the thermal processing method
As the adsorbent recycling based on the conventional thermal processing applies convective heat transfer, it has low drying speed and efficiency. The drying process starts from the surface to the inside, leading to a general recycling performance at higher cost. To further increase the adsorbent recycling effect and efficiency, thermal processing is necessary for the adsorbent, the environmental pressure for thermal processing of adsorbent and gas pressure in the adsorbent needs to be reduced, the thermodynamic equilibrium of gas on the gas–solid interface needs to be changed, and gas desorption ability from the internal surface of the adsorbent needs to be increased. Hence, vacuum heating shall be adopted to increase the adsorbent recycling effect.

a. Experimental steps
① The ex-service polluted adsorbents were grinded in the high-speed vibration grinding machine and then filtered with a 300–500 or higher mesh sieve. ② Ten grams of filtered adsorbents was
collected and placed in the crucible.③ Ten grams of samples was placed in the vacuum fast cold-hot shock test box. The heating program employed a heating temperature of 200°C and heating time of 2 h. Desorbed toxic gases were sealed up in the gas bottles and then sent to the SF₆ recycling plant for further processing.④ The program was started and stopped until vacuum thermal processing was finished.⑤ Data were recorded and experimental apparatus were cleaned.

b. Experimental results and analysis

Variations of specific surface area, specific volume, and bore diameter of adsorbents after vacuum thermal processing in performance recovery experiment under 200°C and different processing times are shown in Figures 6–8 (the red dotted line is the average performance of new unprocessed adsorbent, and the green dotted line is the average performance of adsorbents after vacuum thermal processing). The specific surface area and specific volume become increasingly stable after 2 h of the vacuum thermal processing, indicating that the adsorption performance reaches saturation basically at 2 h of vacuum thermal processing. However, the bore diameter presents a linear growth with the increase of thermal processing time. The bore diameter of the processed absorbents exceeds the average bore diameter of the unprocessed absorbent at 2~2.5 h, indicating that vacuum heating fails to accelerate the adsorbent degradation. Therefore, the optimal vacuum heating time is still 2 h.

It gets conclusions of the vacuum thermal processing of adsorbents from the contrast analysis. Vacuum thermal processing can increase the recovery efficient of the SF₆ adsorbent. The performance recovery rate of the adsorbent reaches approximately 85%—90%.

The optimal heating time of the vacuum thermal processing is 2h.

![Figure 6. Variations of specific surface area of the adsorbent](image1)

![Figure 7. Variations of specific volume of the adsorbent](image2)

![Figure 8. Variations of bore diameter of the adsorbent](image3)

5. Conclusion

The SF₆ adsorbent in the breaker will adsorb abundant water during the service period and adsorb SF₆ degradation products, including H₂O, SOF₂, SO₂, SO₂F₂, SOF₄, SF₆, and HF.
The adsorbent recycling based on heating method can only recover 60% of performance, whereas the vacuum thermal processing can recover approximately 85%–90% of adsorbent performance. The optimal heating time and heating temperature of the vacuum thermal processing are 2 h and 200°C, respectively.

Existing research results demonstrate that vacuum thermal processing can recover the adsorption performance of the adsorbent to a large extent.

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