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Research Article

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Experiment research on the technologies of heat treatment, recycling and regeneration of SF_6 molecular sieve adsorbent

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ABSTRACT

The recycling of SF_6 molecular sieve adsorbent used in high-voltage electrical equipment has favorable economic, social and environmental benefits in power sector. In this study, the methods for regeneration of SF_6 molecular sieve adsorbent were analyzed, proposing that heat treatment is the most economic and effective method, and the regenerating principles were illustrated. Moreover, experiment on heat treatment was made, by combining with infrared spectroscopy to analyze the change of content of the harmful elements in adsorbents, focusing on determination of the temperature and duration of regeneration by heat treatment of SF_6 molecular sieve adsorbent and conducting adsorption isothermal curve test and verification to confirm the desorption capacity of the recycled SF_6 molecular sieve adsorbent. The experiment shows that for the KDHF-03-type molecular sieve adsorbent, which undergone heat treatment at temperature of 200℃ below for 2 hours, 50%-60% of the harmful decomposed gaseous products was removed, and its adsorption capacity was restored to 60% of the original.

Key words: SF6 Adsorbent, Recycling, Heat Treatment, Regeneration Temperature, Regeneration Duration

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INTRODUCTION

SF_6 molecular sieve adsorbent has been used widely in removing the decomposition products in GIS electrical equipment to ensure the safe and stable operation. SF_6 can be decomposed under arc or abnormal partial discharge, producing poisonous and harmful decomposition gases (HF, SO_2, H_2S, SF_4, SOF_2, SO_2F_2, SOF_4, S_2F_{10}, etc.) that erode internal metal elements of equipment and pose damage to equipment performance and personal safety [1]. With the expansion of scale of electrical power system, the consumption of SF6 molecular sieve adsorbent has been increasing, and every year a large amount of SF_6 molecular sieve adsorbent used has been released in the power facility maintenance. Thus, the recycling and regeneration of of SF_6 molecular sieve adsorbent becomes more and more important.

In general, the released SF_6 molecular sieve adsorbent is soaked in alkaline for tens of hours and then buried deeply . This way of treatment is duration and energy consuming, and cannot remove the poisonous and hazardous substances completely, thus causing environmental pollution. Adsorbent regeneration is an effective way to resolve this problem, it refers to a physical or chemical process that realizes separation or decomposition of adsorbates on the surface of absorbent without destroying the original structure of adsorbent, and then recovers the adsorptive property and makes the adsorbent reusable [2]. Currently, the thermal, chemical, biological, microwave radiation and solvent regeneration methods are commonly used. Chemical regeneration can be classified into wet oxidation and Fenton combustion, etc., the former has a higher requirement in equipment while the later can produce a good effect only when the adsorbate can be mineralized. Biological regeneration is time-consuming and only applicable to the organic adsorbates that can easily be biologically decomposed and that have reversible adsorption and are easy for desorption. Therefore, this method has its own limitations. Microwave radiation is a new-type of generation which has been studied widely but used less in practice. Solvent regeneration has a low efficiency, and it cannot completely remove the pollutants but transfer them. Thermal regeneration enjoys a higher rate of regeneration but lower adsorbate selectivity. In this study, the heat treatment regeneration of SF_6 molecular sieve adsorbent was adopted in experimental research, to determine the optimal regeneration temperature and duration of the heat treatment with thermal gravimetric analysis (TGA) and Fourier infrared spectroscopic analysis; to verify the regeneration effect through the isothermal adsorption test. It is relatively economically appropriate to adopt the heat treatment because of lower price of SF_6 molecular sieve adsorbent. Heat treatment regeneration of SF_6 molecular sieve adsorbent is featured by low investment, processing and operating costs, better recycling effect and high security, and has the possibility of recycling and reusing molecular sieve and adsorbent and realizing the energy and time efficiency.

EXPERIMENT SECTION

2.1 Principle of heat treatment

Activated aluminum oxide and molecular sieve are the commonly used adsorbents. At present, as a new-type and efficient SF_6 adsorbent, KDHF-03 type adsorbent has been used the most widely in SF_6 electrical equipment. It can effectively absorb low fluorine compound, acidoid and moisture, and has especially stronger performance in SOF_2, SO_2F_2 and S_2F_{10} adsorption. Essentially, it realizes heat treatment through indirect heating and raising temperature to enhance the vibrational energy of adsorbate molecules, and change the adsorption equilibrium relationship, thus realizing the desorption of adsorbate from adsorbent or thermal decomposition. During the process of heat treatment, adsorption potential energy and adsorption heat are involved.

Absorption potential energy means that adsorbent molecular present electric neutrality because of the atom or atomic group with opposite charges that constitute the adsorbent molecular structure. However, because of non-restriction by an outer layer of atom with opposite charge, the atomic layer in the outermost of the adsorbent shows electrical imbalances, making the adsorbent molecular tend to seize other external molecules to balance its own electrical property. During the process of heat treatment, desorption coefficient of the adsorbate is determined by the absorption potential energy, and ϕ, the absorption potential energy of the adsorbed state under saturation pressure is [3]:

$$-\phi = -\Delta G = \int_{p}^{p_0} V dp = RT \ln \frac{p_0}{p} \qquad (1)$$

Wherein, ΔG stands for the free energy change, p_0 the saturation pressure, p the adsorbent pressure at certain ϕ, V the molar volume, R the molar gas constant and T the temperature.

Adsorption heat refers to heat effect in the adsorption process. During the process of adsorption, the velocity of molecular movement slows down greatly and consequently gives off heat when the gas molecules move to the solid surface. The degree of adsorbability can be measured by adsorption heat: the more adsorption heat, the stronger the adsorbability; and the coefficient of thermal decomposition can also be measured by adsorption heat. In a low coverage situation, the equivalent adsorption heat (ΔH) related to adsorbate-adsorbent interaction potential can be expressed as [4,5]:

$$\Delta H = \phi - RT + F(T) \qquad (2)$$

Wherein, $F(T)$ is originated from adsorbate molecule vibration and translational energy. For monatomic classical oscillator, $F(T) = 3RT/2$.

2.2 Principles for test and verification of the adsorption isothermal curve

With regard to the adsorbent and adsorbate separation, it is primarily important to define adsorption isothermal curve of adsorbent, as the separation process is evaluated according to adsorption isothermal curve, and the effect of temperature in adsorbent activation and regeneration cannot be ignored. As SF_6 decomposition gases in high-voltage electrical equipment are the gas mixture of various substances, whose equation of adsorption isothermal curve can be deduced by the theories of adsorption potential energy and the adsorption heat, i.e. the extended Langmuir equation [6]:

$$q_i = \frac{q_{mi} B_i p_i}{1 + \sum_{j=1}^{n} B_j p_j} \quad (3)$$

Wherein, q denotes the adsorbing capacity, q_m the saturation adsorption capacity, p the total pressure, B the Langmuir constant, presenting an exponential relation with adsorption heat Q ($Q = -\Delta H$).

According to formula (3), such parameters as specific surface area, bore volume, bore diameter can be obtained after SF_6 molecular sieve adsorbent undergone heat treatment. According to these parameters, the effect, removal rate of poisonous elements and durations of adsorptive property can be predicted.

2.3 Methods and General procedure

In the experiment, heat treatment was adopted in the experiment and KDHF-03-type SF_6 adsorbent, which is the most widely used in SF_6 electrical equipment, was taken as the sample, and the three bags of adsorbents released and recycled were divided into three groups, namely Groups A, B and C. Each group contained several part and 10g for each part. In addition, a fire-new sealed group of adsorbent was taken as the control group (Group D), which was also divided into several parts and 10g for each part, specially,

Firstly, TGA was employed to determine the optimal heat treatment temperature. At a certain temperature, chemical substances absorbed inside the adsorbent can be desorbed from the internal surface and result in change of weight. According to the temperature at which the weight was changed and the rate of weight change, the variety of adsorbing substances and the adsorbing capacity can be roughly evaluated. Moreover, according to the temperatures at which the gravimetry change was maximum, the treatment temperatures for the three groups of adsorbents (Groups A, B and C) can be determined, to ensure that substances inside the adsorbent can be removed fundamentally.

Secondly, according to the treatment temperatures determined through TGA, heat treatment of adsorbents was conducted, for 0h (with no treatment), 0.5h and 2h. FTIR infrared analysis meter was used to test the adsorbents of Groups A, B and C that undergone different period of treatment as well as the adsorbent of Group D, to analyze the differences of infrared spectrograms of adsorbents undergone different durations of treatment in a contrastive way. Based on the features of infrared spectrograms of decomposed gases produced by SF_6 dis-connector, desorption variety and quantity obtained in different durations of treatment were determined, and the optimal temperature and the corresponding durations for heat treatment and recycling were obtained [7].At last, test and verification of the adsorption isothermal curves of the three-group adsorbents (Groups A, B and C) that received different durations of treatment and that of the adsorbent of Group D were conducted to determine the percentage of using this heat treatment method to regenerate and restore the ability of the released SF_6 adsorbent. According to nitrogen adsorbing capacities of adsorbents under different voltages, the surface area, bore volumes and bore diameters of all kinds of adsorbents were obtained[8]. There existed differences in surface area, bore volume and bore diameter between the sealed adsorbent and the recycled adsorbent due to the gas absorption; also differences in surface area, bore volume and bore diameter in spite of the same group of adsorbent due to the differences of treatment duration and gas adsorbing capacity. When such parameters as surface area, bore volume and bore diameter of the adsorbents that received heat treatment are close to that of the sealed adsorbents, the temperature and duration of heat treatment of adsorbents have fundamentally reached the goal of adsorbent recycling.

RESULTS AND DISCUSSION

3.1 Determination of the adsorbent treatment temperatures

Adsorbent treatment temperature was obtained by TGA, which is a thermal analysis technique used to measure the mass-temperature relation of the sample under the program controlled temperature, and to study the thermal stability and elements of materials [9]. After being preheated and dried under the controlled temperature of 20-100℃, the adsorbent was grinded and sieved at 300-500 mesh or more. The temperature was rosed constantly from 100℃, and TGA was conducted on the adsorbent of each group that received treatment for 0h, 0.5h and 2h, to obtain TGA data at different treatment durations. The TGA diagrams of absorbents in different groups were compared, shown in Figure 1.

From the experimental results it can be seen that intersections occurred in the TGA curves of the adsorbents in Groups B, C, D and turning points appeared at 200℃, with smaller weight loss rates, indicating that desorption of the gas adsorbed has been completed at 200℃;

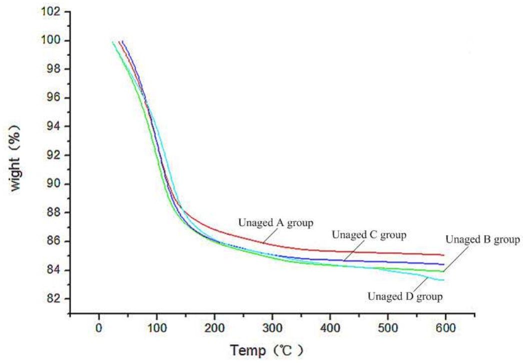

Fig. 1 TGA Comparison Chart of Adsorbent

below 200℃, the weight loss rates of adsorbents in Groups A, B, C were all bigger than that of unsealed adsorbent, indicating that in this temperature range desorption of the gas adsorbed on the adsorbents happened, indirectly showing that the hyperthermic treatment was effective to the adsorbent recycling, also, with the rising of temperature, the weight loss ratio of adsorbent became smaller after 200℃, showing that after 200℃, improvement of the adsorbent recycling effect was unobvious by rising the treatment temperature.

3.2 Determination of the absorbent treatment durations

Chemical composition analysis was made on the adsorbents of Groups A, B and C that undergone heat treatment for the durations of 0h, 0.5h and 2h, respectively and the adsorbent of Group D by using FTIR, to get the Fourier infrared spectra of the four Groups, which were comparatively analyzed. Group A was taken as the example, a comparative analysis on the infrared spectrograms of Group A and Group D was made, as shown in Figure 2. It can be seen that the adsorbent in Group A without receiving heat treatment has obvious absorption peaks at 758cm^{-1}, 680cm^{-1}, 569cm^{-1}, 460cm$^{-1,}$ 448cm^{-1}. By comparing with the infrared spectrum adsorbent wave data of SF_6 gas decomposition products (Table 1) and taking the measurement errors due to the drift of peak in the process of the infrared spectrum analysis into consideration [10-12], it was found that the absorption peaks of Group A were the decomposition products of temperature range desorption of the gas adsorbed on the adsorbents happened, indirectly showing that the hyperthermic treatment was effective to the adsorbent recycling, also, with the rising of temperature, the weight loss ratio of adsorbent became smaller after 200℃, showing that after 200℃, improvement of the adsorbent recycling effect was unobvious by rising the treatment temperature.

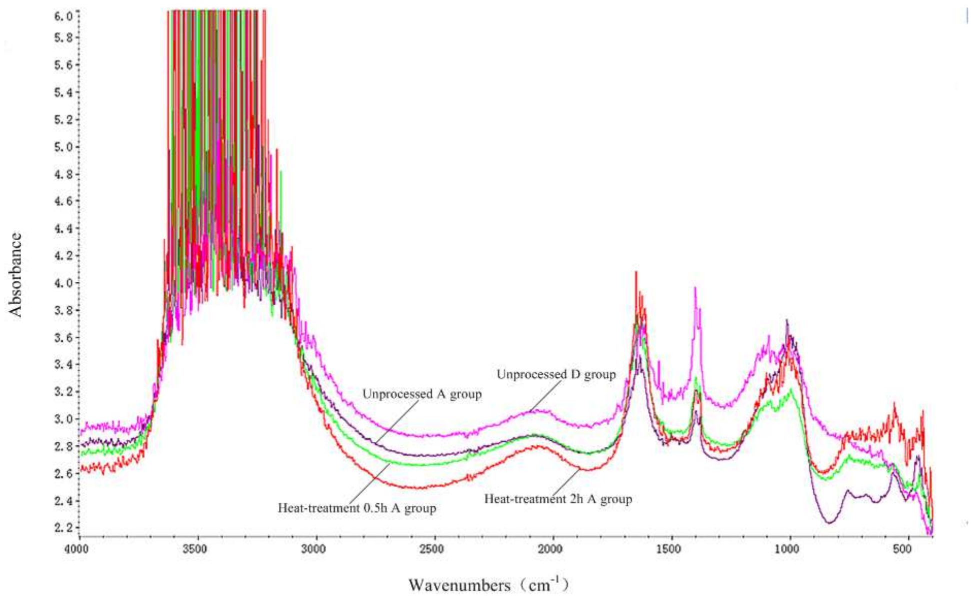

Fig.2 FTIR Comparison between Group A and D

3.3 Determination of the absorbent treatment durations

Chemical composition analysis was made on the adsorbents of Groups A, B and C that undergone heat treatment for the durations of 0h, 0.5h and 2h, respectively and the adsorbent of Group D by using FTIR, to get the Fourier infrared spectra of the four Groups, which were comparatively analyzed. Group A was taken as the example, a comparative analysis on the infrared spectrograms of Group A and Group D was made, as shown in Figure 2. It can be seen that the adsorbent in Group A without receiving heat treatment has obvious absorption peaks at 758cm^{-1}, 680cm^{-1}, 569cm^{-1}, 460cm$^{-1,}$ 448cm^{-1}. By comparing with the infrared spectrum adsorbent wave data of SF_6 gas decomposition products (Table 1) and taking the measurement errors due to the drift of peak in the process of the infrared spectrum analysis into consideration [10-12], it was found that the absorption peaks of Group A were the decomposition products of SF_6 including SOF_4, SF_4, SO_2F_2, SOF_2, etc., and the adsorbent in Group A might have adsorbed the decomposition products described above. With the extension of the treatment duration, the absorption peaks of corresponding decomposition products such as SOF_4 and SF_4 disappeared and the adsorption peaks of other decomposition products were significantly reduced, showing that in this process the chemical bond of sulfur based functional groups of sulfide broke and was released in a form of desorbed gas [13]. The measured data shows that removal ratio of the decomposition products of harmful gases of SF_6 was about 50%-60%, indicating that under the heat treatment condition with heating temperature of 200℃ and heating duration of 2h, the SF6 decomposition products of the adsorbents were significantly reduced.

Tab.1 Infrared spectrum absorption wave data of SF_6 gas decomposition products

Gas	Wavenumber/cm^{-1}
SOF_2	530,1330,1340
SO_2F_2	539,544,552
SOF_4	752,829.7
SO_2	1167,1360
SF_4	746
CF_4	1280,1283
HF	3644
CO	2169
SF_6	610,946,1270,1595,1720

3.4 Test and verification of adsorbent regeneration

Specific surface area and bore size of adsorbents with different amounts of gas adsorption are different. The optimum treatment durations were obtained by testing the adsorption isotherm parameters of the adsorbents at the same treatment temperature and different treatment durations, respectively [14,15]. In this study, the specific surface area, specific volume and bore diameter (Table 2) of the adsorbents of Group A and Group D that undergone no heat treatment and that undergone heat treatment at 200℃ for 0.5 to 12h were comparatively analyzed, finding that adsorption and regeneration ability of the adsorbent that received 2h heat treatment at 200℃ has reached the optimum, the recycled adsorptive capacity reached about 60%.

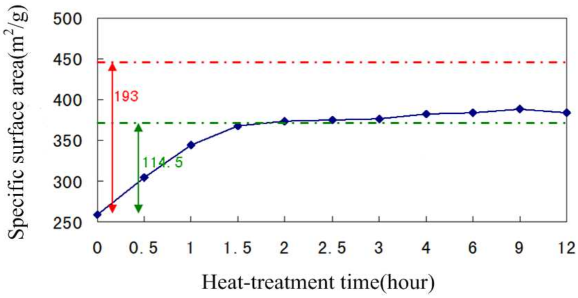

Fig.3 Specific Surface Area Trend of the Adsorbent

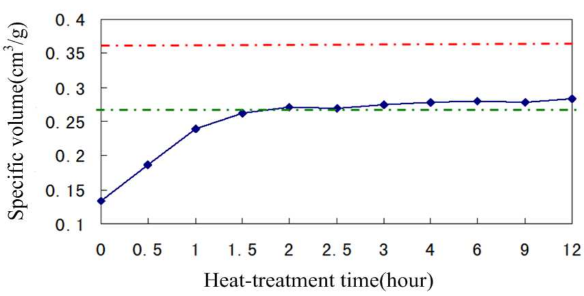

Fig.4 Specific volume Trend of the Adsorbent

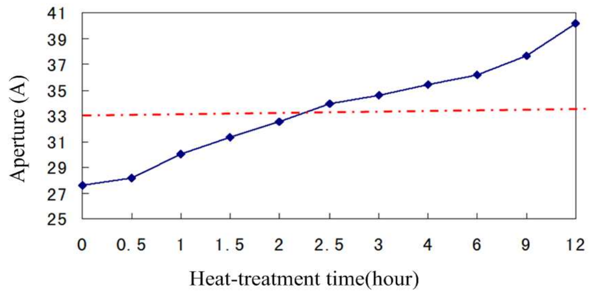

Fig.5 Trend of Bore Diameter Change of the Adsorbent

Table 2 Parameters of Adsorbents at 200 ℃ at Different Heat Treatment Durations

	Group A						Group D					
	—	0.5h	2h	4h	8h	12h	—	0.5h	2h	4h	8h	12h
Specific Surface Area (m^2/g)	259.42	264.52	278.28	318.28	339.52	380.52	166.81	171.82	186.82	206.82	246.82	290.82
Specific Volume (cm^3/g)	0.1857	0.1861	0.2147	0.2147	0.1861	0.1861	0.1468	0.1468	0.1468	0.1468	0.1468	0.1468
Bore (A)	28.634	28.148	30.874	32.874	36.148	40.148	35.199	35.258	37.199	39.199	44.255	40.844

However, with the extension of the heat treatment duration, the adsorptive capacity was increased slightly. Figure 3, Figure 4 and Figure 5 respectively show the trends of the specific surface area, bore volume, and bore diameter change of the adsorbent of Group A that were treated at 200℃ for different durations .Adsorbents of Groups B and C were also tested. By analyzing the heat treatment effects on the adsorbents of Groups A , B and C, it was found that after heat treatment the specific surface area, bore volume and bore size of the adsorbents of three groups followed similar trends, indicating that phenomenon of restoring adsorption capacity of the adsorbents that received heat treatment at 200℃ for 2h to up to 60% is universal.

Currently, the research on recycling and regenerating the SF_6 adsorbent is still relatively rare both at home and abroad. The research of heat treatment based SF_6 adsorbent recycling and regeneration technology proposed in this paper can be considered as a primary exploration in this regard. From the perspective of experimental results, the technology is cost-saving and environment-friendly, and can ensure stable performance of the regeneration of SF_6 adsorbent.

CONCLUSION

An experimental study of the recycling and regeneration of SF_6 adsorbent by the heat treatment method was conducted, the regeneration temperature was determined based on the most widely used and technologically sophisticated thermal regeneration principle and TGA, and the regeneration duration was determined by FTIR. Thus, the optimum regeneration temperature and the optimal treatment duration of SF_6 adsorbent were obtained. Also, an adsorption isotherm curve test has been done to validate the results. The results show that through the 2h heat treatment at 200℃, 50%-60% of the harmful decomposition gas products of SF_6 adsorbent was removed, and the adsorption capacity could be restored to about 60% of the original.

Through the experimental research on heat treatment based recycling and regeneration of SF_6 adsorbent, the optimum heating temperature and treatment duration for heat treatment of SF_6 adsorbent were obtained, which will be conducive to reducing the recycling energy cost and time cost on the basis of ensuring the recycling effect.

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