Influence of Humidity on Adsorption Performance of Activated Carbon

Fukai He*, Jigang Zhang, Aiming Liu, Guozhen Zhu

Shangdong Nuclear Power Company, Shandong, China

Abstract: Activated carbon filter is the main equipment used to remove pollutants in the ventilation system in a nuclear power plant. Its main function is to remove radioactive iodine to minimize radioactive hazards against workers in the ventilation area. Periodic evaluation is a key step for verifying its operation effectiveness, further to ensure the safety and long-term operation. In this paper, by changing the micropore structure and surface chemical properties of activated carbon, its physicochemical properties and adsorption performance against methyl iodide under the high humidity working environment are studied. The results show that the adsorption performance of activated carbon on organic compound decreases significantly under the high humidity conditions; however, the combination of potassium iodide, triethylene diamine and functional groups on the activated carbon surface form stable chemical bonds and a new surface structure, which enhances the adsorption performance and stability of activated carbon against pollutants and makes it difficult to remove pollutants. The adsorption capacity of nuclear activated carbon can be restored to 80.7% of the initial capacity, and the adsorption performance can be obviously improved.

Keywords: Nuclear activated carbon filter; radioactive iodine; physicochemical properties; microstructure; adsorption efficiency.

1. Introduction

The leakage and diffusion of radioactive particles will seriously affect the accident site and surrounding areas, and even the global ecological environment. Particulate pollutants are difficult to settle and capture in the air due to the small size, resulting in long-term air pollution. It is easy to be inhaled into the deep respiratory tract with the air, which aggravates the harm to the human body. It is extremely urgent to deal with radioactive particulate pollutants.

In view of the source and harm of radioactive particles from the nuclear island, a sound filtration and purification safety system is adopted to fully send fresh air into the atmosphere and enhance the ventilation effect, improve the air quality, and effectively and reasonably control the content of particulate pollutants around the workplace in the nuclear island[1]. As a high-quality adsorption material, the activated carbon is a kind of carbon-based adsorption material with rich pore structure, huge specific surface area, strong adsorption capacity, good chemical stability, and high mechanical strength.

The research shows that there is a certain competition between organic compounds, such as benzene, and water vapor on the adsorption of activated carbon under different humidity conditions. When the relative humidity is low (10 ~ 30%), the competition is not obvious; when the relative humidity is 50% or above, the water vapor will obviously inhibit the adsorption of benzene. According to technical requirements, the activated carbon is stored at the humidity below 70%, but the onsite humidity in summer is 80 ~ 90%, where a large amount of water vapor exist in the environment, which reduces the adsorption effect of activated carbon[2]. The ventilation and filtration system in the main control room provides air filtration to control the airborne radioactivity status. However, in the high humidity season summer, the humidity in the cabinet chamber of the ventilation unit is higher than 70% and even above 90% RH in severe case, which affects the adsorption efficiency of the activated carbon filter and challenges the radioactivity control of the defense-in-depth function of the system; at the same time, there are also related risks in the air filtration system of safety cover during refueling and overhaul under the high humidity in summer, it is of great significance to analyze the adsorption effect and recycling period of activated carbon on radioactive particles in high humidity environment[3], providing strategy support for the normal operation of ventilation system in the power station.

* Corresponding author: hefukai91@163.com

2. Experimental Materials and Methods

2.1 Test Plans under Different Humidity Conditions

Thermostat, saturated H_2O steam preparation and loading equipment, dry air input equipment and humidity detector. There are 4 independent humidity control units, each is of 40cm*40cm*40cm specification; they share a set of temperature control with insulation layer and high-precision temperature detection and heating; each unit independently measures humidity; the air with humidity above 95% of vacuum is injected to increase the humidity, and the dry nitrogen is injected to reduce the humidity[4]. The influencing processes of different humidity are explored: four units are respectively set as control group, 70% humidity group, 80% humidity group, and above 90% humidity group, put 3-5 pieces of 50g activated carbon per unit. In the first stage of short-term 5-day influence, the activated carbon was obtained in 1st, 2nd, 3rd and 5th day for the performance evaluation[4]. According to the 5-day test, the second stage of long-time 30-day influence test was carried out, and the activated carbon was obtained at the 10th, 20th and 30th day respectively for performance evaluation. Humidity affects the adsorption capacity of radioactive particles. According to the standard test regulations, use the activated carbon affected by long-term humidity for the adsorption performance test of methyl iodide at 30 ℃ and RH95%; dry the activated carbon affected by humidity at 105 ℃ for 1h, and carry out the adsorption performance test of RH95% methyl iodide at 30 ℃ and RH95% to evaluate the performance of activated carbon.

2.2 Adsorption Performance Test of Activated Carbon

After fully oscillating and integrating of certain sample and iodine solution, the residual iodine in the filtrate is titrated with sodium thiosulfate solution. The amount of iodine adsorbed per gram of carbon (in milligrams) in the residual iodine solution at the concentration of 0.02 mol/L (1/2 I_2) shall be determined as the iodine value[5] .

Make the air carrying carbon tetrachloride flow through the activated carbon sample with known mass under specified conditions until the mass of the carbon sample no longer increases, and then determine the mass of carbon tetrachloride in the sample to evaluate the adsorption rate of activated carbon on carbon tetrachloride[6].

Under the specified test conditions, place the sample in an adsorber filled with benzene vapor at constant temperature of (25±1) ℃ for 24 hours, take 1 g (accurate to 0.0001 g) of sample, and immediately put evenly on the bottom of a high-type weighing bottle with constant weight set up in advance. Accurately take 100 mL benzene in a fume hood and add it to an adsorber[7]. Put the high-type weighing bottle containing the sample on the grid of the adsorber, place the adsorber in the incubator at (25±1) ℃ for 24 hours, put the cover on the high-type weighing bottle, take it out and weigh it.

CH3I adsorption tests under different conditions can be divided into three parts: in the first part, use CH3I/N2 air product and mass flow controllers (using air as diluent gas) to generate constant and reproducible CH3I concentrations[8]. The second part is called a “reactor system” in which a given CH3I concentration is kept in contact with a fixed activated carbon mass under various conditions (temperature (T) and relative humidity (RH)). Depending on the required information (adsorption kinetics/adsorption isotherms), one reactor or multiple reactors consisting of gas chromatograph and pulse discharge helium ionization detector[11] can be used in this part. The analysis parameters are optimized to ensure significant signal-to-noise ratio and sufficient temporal resolution for fine monitoring of CH3I dynamic attenuation.

3. Results and Discussion

3.1 Influence on Physical Properties of Nuclear Activated Carbon under the High Humidity

3.1.1. Test of Moisture Content, Ash Content and Bulk Density

The bulk density of activated carbon is affected by many factors, including humidity. Generally, humidity will affect the density of activated carbon to a certain extent. Under the high humidity environment, the bulk density of activated carbon will decrease[10]. Because the activated carbon surface will adsorb water under the high humidity, resulting in an increase in viscosity between particles and a decrease in bulk density; in low humidity environment, the bulk density of activated carbon will increase. This is because activated carbon is not easy to absorb water on the surface under low humidity, and its volume is not easy to expand. Therefore, under the same volume, more activated carbon can be accumulated to increase its density.

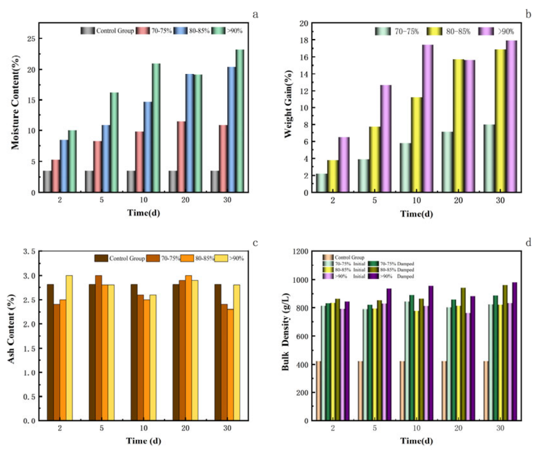

Fig. 1 Changes of moisture content, weight gain, ash content and bulk density

With the increase of time, the bulk density of nuclear activated carbon increase gradually and slowly, which indicates that activated carbon impregnated with potassium iodide and triethylene diamine occupies the spot of adsorbing water, and the gap between activated carbon particles becomes smaller, thus improving the adsorption performance[11]. At the same time, the physical strength of activated carbon is improved to make it more durable. During impregnation, the moisture content of activated carbon will gradually increase, because the impregnation solution will gradually penetrate into the pores of activated carbon and occupy a part of space, thus increasing the moisture content of activated carbon. However, with the impregnation, the water content in the pores of activated carbon will be gradually replaced, thus reducing the water content gradually. After impregnation, the moisture content will depend on the environment. If the activated carbon is in a dry environment, the moisture content will further decrease, otherwise it will increase.

The ash content of activated carbon refers to the content of non-combustible inorganic substances in activated carbon[8]. Activated carbon is usually made by heating carbonaceous materials at high temperature, which will remove organic materials, but will not remove inorganic materials. Therefore, activated carbon will contain a certain number of inorganic substances, such as minerals, oxides, etc. The content of inorganic substances is called the ash content of activated carbon. Ash content is an important index of the quality of activated carbon, because the lower the ash content, the better the adsorption performance of activated carbon[13]. The results show that when the relative humidity is above 80%, the ash content of activated carbon does not increase significantly, or the increasing speed is relatively slow. It may take long-term exposure to high humidity to cause obvious changes.

3.1.2. Specific Surface Area Test

The specific surface area of activated carbon will decrease with the increase of humidity, because water will fill pores and occupy part of the surface area. When the humidity is low, the quantity of water molecules on the activated carbon surface is small, and the specific surface area of the activated carbon is high. However, with the increase of humidity, the quantity of water molecules on the activated carbon surface will increase, which will reduce the surface area available for adsorption and lead to the decrease of specific surface area[17]. In some cases, for instance, under the high humidity, the pore structure of activated carbon may collapse due to the occupation of water molecules, thus further reducing the specific surface area.

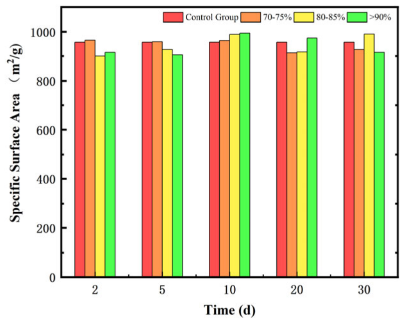

Fig. 2 Changes of specific surface areas before and after drying with different humidity

Impregnated activated carbon changes smoothly under different humidity conditions, and the specific surface area of activated carbon will decrease with the increase of humidity, because water will fill pores and occupy a part of the surface area. Specifically, when the humidity is low, the number of water molecules on the activated carbon surface is small, so the specific surface area of activated carbon is high. However, with the increase of humidity, the amount of water molecules on the activated carbon surface will increase, which will reduce the surface area available for adsorption and lead to the decrease of specific surface area[14]. In some cases, for instance, under the high humidity the pore structure of activated carbon may collapse due to the occupation of water molecules, thus further reducing the specific surface area. Adsorption properties of activated carbon under different humidity.

3.1.3. Adsorption of Iodine, CCl4 and Benzene under Different Humidity

As shown in the following figure, the adsorption performance of activated carbon after impregnation changes greatly at above RH90%. When the relative humidity is more than 90% and the time period is 5 days, the adsorption performance of activated carbon is 30mg/g different from that of control group. The addition of potassium iodide can increase the iodine ion content on the activated carbon surface, thus improving the iodine adsorption efficiency. Potassium iodide can increase the adsorption sites and promote the adsorption and fixation of iodine ions on the activated carbon surface[16]. The addition of triethylenediamine can increase the content of amino groups on the activated carbon surface, thus increasing the adsorption sites and improving the adsorption efficiency of iodine. In addition, triethylenediamine can also form chemical bonds with iodine, which increases the selective adsorption of iodine by activated carbon. The combined use of potassium iodide and triethylenediamine can produce synergistic effect and improve the adsorption efficiency and selectivity of activated carbon for iodine.

CCl4 adsorption rate (activity) is an important physical index for screening and evaluating nuclear activated carbon.

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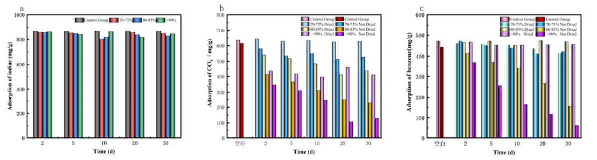

Fig. 3 Adsorption of iodine, CCl4 and benzene under different humidity

It is required that the adsorption rate of CCl4 used in ventilation and purification system of nuclear facilities should not be less than 60%[16]. The figure shows the change of CCl4 adsorption performance of activated carbon impregnated under different humidity. When the relative humidity is more than 90%, the adsorption performance of dried activated carbon on benzene is 34.08% higher than that of undried activated carbon, and when the relative humidity is 80 ~ 85%, the adsorption performance of dried activated carbon on benzene is about 42.19% higher than that of undried activated carbon. When the relative humidity is 70 ~ 75%, the adsorption performance of dried activated carbon on benzene is about 17.38% higher than that of undried activated carbon.

The results show that impregnated activated carbon has poor adsorption performance for carbon tetrachloride. Under different humidity conditions, the adsorption performance of impregnated activated carbon has been significantly reduced after continuous use. On the one hand, moisture can occupy the space in the pores of activated carbon, which limits its adsorption performance. The adsorption load of activated carbon increases with time, and the activated carbon surface is gradually covered by pollutants, thus reducing its adsorption efficiency for carbon tetrachloride.

At RH80 ~ 85%, the change of adsorption performance of dried activated carbon on benzene is opposite to that of the undried activated carbon. The possible reason is that the potassium iodide and triethylenediamine can increase the functional groups on the activated carbon surface, thus improving its ability to adsorb benzene molecules. Potassium iodide can increase oxidation functional groups on the activated carbon surface, while triethylenediamine can increase amine functional groups. These functional groups can interact with benzene molecules, thus improving the adsorption performance.

3.2 Study on Adsorption Performance of Activated Carbon against Methyl Iodide in High Humidity Environment

In dry environment, the air humidity is low, which may affect the pore structure and adsorption performance of activated carbon. Therefore, it is necessary to control the temperature and humidity during the experiment to simulate the dry environment[18]. In the figure, it can be seen that the adsorption performance of dried activated carbon against methyl iodide is 80.8% higher than that of undried activated carbon at above RH90%, the adsorption performance of dried activated carbon against methyl iodide is about 89.8% higher than that of undried activated carbon at RH80 ~ 85%, and the adsorption performance of dried activated carbon against methyl iodide is about 93.8% higher than that of undried activated carbon at RH70~75%.

When the effective contact area between impregnated activated carbon and methyl iodide, volume diffusion rate, pore diffusion rate and flow rate of methyl iodide are fixed, the number of methyl iodide molecules that can be effectively adsorbed is fixed. The high concentration of methyl iodide at the inlet means that more methyl iodides penetrate the activated carbon layer, which leads to the decrease of adsorption efficiency of activated carbon.

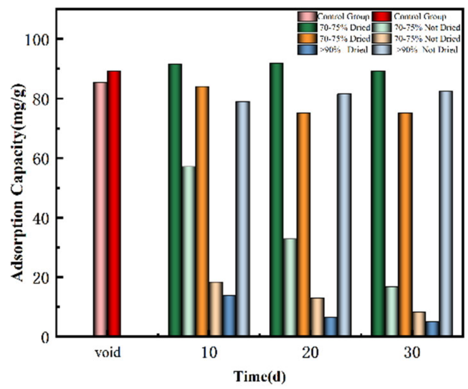

Fig. 4 Comparison of adsorption of methyl iodide before and after drying under different humidity in dry environment

Impregnating agent can not only occupy the active site of activated carbon to reduce the physical adsorption performance of activated carbon, but also form a complex with methyl iodide to improve the chemical adsorption performance of activated carbon[19]. Therefore, there must be an optimal value of impregnation amount, which optimizes the sum of physical adsorption capacity and chemical adsorption capacity of impregnated activated carbon. In this experiment, the negative value of electric mobility of activated carbon particles will become larger, that is, the electronegativity of activated carbon particles will increase, resulting in the increase of ionization potential. According to the potential energy relation of dispersion action[20], adsorption and desorption of activated carbon modified by ionization of carbon particles on radioactive methyl iodide with constant adsorbate molecules will increase the dispersion force of carbon particles. Because the physical adsorption of activated carbon against methyl iodide is mainly realized by the dispersion force, the adsorption efficiency of activated carbon against methyl iodide will be improved with the increase[20]; When the prepared impregnated activated carbon is not dried, on the one hand, a small amount of impregnated solution will stay on the outer surface of the activated carbon, blocking part of the orifice, reducing the channel for methyl iodine molecules to enter the inside of the activated carbon and reducing the adsorption efficiency; on the other hand, the water molecules in the impregnant will occupy more effective adsorption sites, reducing the adsorption sites that can effectively adsorb methyl iodide molecules. If the drying time is too long (the activated carbon surface turns white), some oxygen-containing groups on the activated carbon surface will be decomposed by heat, which will reduce the number of surface groups that play an important role in the adsorption of activated carbon and reduce the adsorption performance.

4. Conclusion

The adsorption performance of different activated carbons under the high humidity condition is tested and analyzed. The physical and chemical properties of activated carbon before and after modification are studied by means of pore structure test, scanning electron microscope, EDS analysis and Boehm titration, and the adsorption properties of modified activated carbon against gaseous iodine under different environmental factors are analyzed by adsorption experiments. We make the following conclusions:

(1) When the relative humidity is 90%, the adsorption rate of activated carbon against methyl iodide will decrease with the time increase, and the water content will increase accordingly. After adsorption of activated carbon reaches equilibrium, under the same humidity, the moisture content of impregnated activated carbon is lower. And with the increase of relative humidity, the difference of moisture content of activated carbon before and after impregnation is larger, and the maximum reaches 31%.

(2) After the 20-day influence of humidity, the concentration of methyl iodide is 0.58 mg/L, the adsorption rate of methyl iodide is 69.9%, which is 30% lower than that of activated carbon in the control group; after the 65-day influence of humidity, the adsorption rate is 24.1% when the concentration of methyl iodide is 1.32 mg/L; the adsorption efficiency of dried activated carbon affected by 90% humidity for 20 days against methyl iodide is 98.9%, which is 28.9% higher than that of undried activated carbon; the adsorption efficiency of dried activated carbon affected by humidity for 60 days against methyl iodide is 97.7%, which is 73.53% higher than that of undried activated carbon.

(3) The acidic functional groups on the activated carbon surface decrease, the basic functional groups increase, and the pH value increases. The decrease of the total amount of groups provides adsorption pores for the adsorption of gaseous iodine. With the decrease of oxygen-containing functional groups, the number of basic functional groups increases, and the non-polar basic functional groups also increase the adsorption performance of activated carbon on iodine (non-polar).

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