Study on the water vapor adsorption Characteristics of Carbon materials in HTGR

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Abstract. High-temperature gas-cooled reactor (HTGR) is the first kind of power plant with fourth-generation features in the world, and a large amount of graphite and carbon material is adopted as structural material and fuel matrix material, including boron-containing carbon (BC) and isostatic pressure graphite (IG-110). As a kind of porous material, the carbon material contains a certain amount of moisture, which will impose negative effects on reactor safety. Therefore, this paper studies the water vapor adsorption characteristics of carbon materials in HTGR. The adsorption isotherms of BC and IG-110 were obtained by experimental measurements. Experiments show that the moisture adsorption of IG-110 is much lower than that of BC at various relative humidity. The experimental data is analysed by the BET, GAB, D-A, Oswin adsorption models.

1. Introduction

High-temperature gas-cooled reactor (HTGR) is the first kind of power plant with fourth-generation features in the world, and a large amount of graphite and carbon material is adopted as structural material and fuel matrix material, including boron-containing carbon (BC) and isostatic pressure graphite (IG-110) [1]. As a kind of porous material, there are many micro pores in it, and therefore absorbs moisture through pores from surroundings at room temperature. The specific surface area of carbon material is very high, and the main absorption type is physical absorption.

The moisture in carbon materials will be released into the helium coolant during the temperature-rise process of reactor. There is about 60t of graphite material used in the HTR-10 [2], and almost 1000t in a single reactor core of HTR-PM [3]. Approximately 100t of graphite is used in AVR in Germany and 700kg of water is released during its power-rise and temperature-rise process. In HTR-10, about 130kg of water is released.

The chemical corrosion reaction between graphite and moisture exists in the high-temperature condition in an operating reactor, and therefore imposes bad influence on material strength and service life. Especially in the case of air and water leakage under nuclear power accident conditions, the corrosion is even more serious [4]. In order to decrease the corrosion, the reactor construction, fuel and graphite spheres and the space of primary system shall be heated and dehumidified. The limiting value of moisture content in helium coolant is 2cm$^3$/m$^3$ [5]. Therefore, study on the water vapor adsorption characteristics of carbon materials in HTGR is essential.
Numerous studies have investigated water vapor adsorption on various porous medium. With the different relative pressures, the adsorption forms of the adsorbates (water vapor) in the porous material structure are different. When the relative pressure is very low, water vapor molecules are first captured by the adsorption active center on the surface of the material, and then form monomolecular adsorption layer[6]. When the relative pressure rises to a certain value, the water vapor will undergo capillary condensation in the pore structure of the material[7]. As the further increases of relative pressure, the pore structure of the material will be gradually filled with water vapor.

The International Uniform of Pure and Applied Chemistry (IUPAC) classifies the pore sizes as follows: micropore (< 2 nm), mesopore (2-50 nm) and macropore (>50 nm). Different materials exhibit different adsorption isotherms corresponding to their pore sizes. Although different materials exhibit different adsorption isotherms, the adsorption isotherms of most materials can be classified into 5-6 types, as shown in Figure 1[8]. Type I is characteristic for purely microporous material, such as zeolite or activated carbon. Type II for pure nanoporous or macroporous material. Type III for the rare cases of nonporous materials with small interaction between adsorbent and adsorbate. Type IV for common mesoporous material, while type V presents relatively rare mesoporous materials, which is also due to the small interaction between adsorbent and adsorbate. Type VI is quite rare, the adsorption process is carried out step by step.

![Figure 1. The original types of isotherms formulated by IUPAC.](image)

In 1916, Langmuir proposed the theory of monolayer adsorption, which satisfactorily explained the type I adsorption isotherm [9]. He regarded the adsorption equilibrium as a dynamic equilibrium. That is, the gas or vapor molecule impacts the solid surface, and stays on the gas surface for a certain time, and then gets enough energy to break away from the surface and desorption occurs. Brunauer, Emmett and Teller put forward the theory of multilayer adsorption based on Langmuir equation in 1938, and deduced the BET equation [10], which has more general applicability. Later studies have found that for most materials, the assumptions of the BET model are not completely correct. What’s more, this model is only applicable within the limited humidity range of 5 %RH to 35%RH. In 1946, Oswin developed an empirical model formula [11]. Although there are relatively few literature reports using the Oswin model equation, its fitting effect on the experimental data of food isothermal moisture absorption is better than the BET formula in most cases. In the 1980s, based on the Langmuir single-molecule adsorption equation and the BET equation, Guggenheim, Anderson, and De Boer introduced additional degrees of freedom and deduced the three-parameter GAB equation in which the adsorption layer is multimolecular layer [12]. The GAB equation, which apply to 0-90% RH, has been considered as the most general adsorption model formula since it was proposed.
For the carbon materials BC and IG-110 used in high temperature reactor, some studies have been carried out on their hygroscopicity. The results show that the equilibrium moisture absorption of BC is only about 0.1% [13]. The moisture absorption is closely related to the humidity of the environment, and the more moderate the equilibrium moisture content is, the greater the equilibrium moisture content is. These studies have some limitations, and haven’t measured the complete adsorption isotherms of BC and IG-110 for water vapor. In this paper, the phenomena of water vapor adsorption and desorption of BC and IG-110 are detailed studied, and the water vapor adsorption isotherms of samples are measured.

2. Materials and Methods

2.1. Materials

The first high temperature gas-cooled experimental reactor HTR-10 is built in 2000 [14], which used more than 60 tons of carbon materials in its core. The BC material was provided by FANGDA Carbon New Material Co., LTD, China, and IG-110 was provided by TOYO TANSO Co., LTD, Japan. The experimental samples are shown in Figure 2. The cylindrical samples are both 10mm in diameter and 5mm in height.

Pore parameters of BC and IG-110 measured by mercury intrusion method and Nitrogen adsorption method are shown in Table 1.

Table 1. Pore parameters of BC and IG-110.

| Parameter          | BC            | IG-110        | Unit   |
|--------------------|---------------|---------------|--------|
| Size D10*H5        | D10*H5        | mm            |
| Weight             | 726.296       | 736.414       | mg     |
| Volume Density     | 1.7468        | 1.8259        | g/cm³  |
| Apparent Density   | 2.0295        | 2.1560        | g/cm³  |
| Porosity           | 13.93         | 15.31         | %      |
| Specific surface area | 12.581     | 15.198        | m²/g   |
| Most probable aperture | 7930       | 1716          | nm     |

2.2. Methods

The dynamic water vapor absorption instrument (DVS Adventure, Surface Measurement Systems, England) was used to the water vapor absorption and desorption test. The samples were first cleaned by ethanol, then dried in a drying oven at 250 °C for 12 hours, and then cooled to environment temperature in a glass vessel containing silica gel desiccant. After drying, the samples were put into the climatic chamber of the DVS instrument and placed on the metal pallet, and the automatic balance will weigh pallet precisely at regular intervals. The parameters of the water vapor absorption test are shown in Table 2.

Table 2. Water vapor absorption test parameters.

| Parameter             | Value        | Unit  |
|-----------------------|--------------|-------|
| Temperature           | 5-85         | °C    |
| Max. weighing capacity | 1500         | mg    |
| Weighing precision    | 0.0001       | mg    |
| Relative humidity cycle | 0-98 (5-60°C)| %     |
| Relative humidity cycle | 0-85 (5-60°C)| %     |

For each experiment the sample of BC and IG-110 were used for water sorption analysis. Using the multistep technique adsorption isotherms for each sample were obtained at 20 °C. Under each humidity,
it is considered to have reached equilibrium when the mass change rate is less than 0.0002% within 15 minutes.

3. Experimental results and analysis

3.1. Modelling of sorption isotherms

The adsorption data is analysed for various adsorption models which include: (i) Brunauer–Emmett–Teller (BET); (ii) Dubinin–Astakhov (D–A)[15]; (iii) Oswin (iv) Guggenhem, Anderson, and De Boer (GAB). The corresponding mathematical expression for adsorption models are given in Table 3.

| Model       | Mathematical expression                                                                 | Estimated parameters |
|-------------|-----------------------------------------------------------------------------------------|----------------------|
| BET         | $M = \frac{M_m C (P/P_0)}{[1-(P/P_0)](1-(P/P_0)) + C (P/P_0)}$                         | $M_m, C$             |
| D-A         | $M = M_0 \exp \left[ -\left( \frac{RT \ln (P/P_0)}{E} \right)^n \right]$               | $M_0, n, E$          |
| Oswin       | $M = A \left( \frac{P/P_0}{1-(P/P_0)} \right)^B$                                        | $A, B$               |
| GAB         | $M = \frac{M_m C_{GAB} K (P/P_0)}{[1-K(P/P_0)](1-K(P/P_0)) + C_{GAB} K (P/P_0)}$         | $M_m, C_{GAB}, K$    |

3.2. Fitting of adsorption isotherm

The values of obtained fitting parameters of samples of BC and IG-110 are given in Table 4. The parameters of each model are identified in the nomenclature. Linear technique is used to determine the model parameters and goodness of the fit by minimizing the mean relative percentage deviation modulus, E (%) which is defined as[16]:

$$E(\%) = 100 \times \frac{1}{N} \sum_{i=1}^{N} \left[ \frac{M_e - M_c}{M_e} \right]$$

Where N is the number of experimental points, $M_e$ is experimental and $M_c$ is calculated adsorption uptakes (g/kg).

| Model       | Estimated parameters | BC          | IG-110       |
|-------------|----------------------|-------------|--------------|
| BET         | $M_m$ (g/kg)         | 0.0836      | 0.0161       |
|             | $C$                  | 5.3449      | 3.7028       |
|             | $R^2$                | 0.9992      | 0.9996       |
|             | $E$ (%)              | 13.47       | 20.25        |
| D-A         | $M_0$ (g/kg)         | 4.8563      | 1.2694       |
The table below shows the results of the adsorption process for different materials and models:

| Model | Parameter | Value 1 | Value 2 |
|-------|-----------|---------|---------|
|       | n         | 0.3     | 0.3     |
|       | E (kJ/kg) | 1.4319  | 1.2306  |
|       | $R^2$     | 0.9998  | 0.9999  |
|       | E (%)     | 4.43    | 7.24    |
| Oswin | A         | 0.1503  | 0.0355  |
|       | B         | 0.6809  | 0.6670  |
|       | $R^2$     | 0.9998  | 0.9999  |
|       | E (%)     | 5.47    | 8.17    |
| GAB   | $M_m$ (g/kg) | 0.0985 | 0.0229 |
|       | $C_{GAB}$ | 4.1938  | 4.1973  |
|       | K         | 0.9555  | 0.9549  |
|       | $R^2$     | 0.9998  | 0.9999  |
|       | E (%)     | 3.92    | 5.45    |

$R^2$ is the coefficient of determination.

Figure 2 and Figure 3 show the experimentally measured adsorption isotherms data for the BC and IG-110 material respectively, together with their fits using the BET, GAB and D-A theoretical model. As seen in Figure 2, BET, GAB and D-A equation can fit the experimental data of BC well at low relative humidity, but in high relative humidity, the prediction accuracy of BET is obviously lower than that of GAB and D-A model.

4. Conclusions

Figure 3 shows that the equilibrium adsorption capacity of IG-110 for water vapor is much lower than that of BC. The GAB and D-A equation can well simulate the trend of experimental data for IG-110, which is much better than the BET equation.
The adsorption isotherms of BC and IG-110 were obtained by experimental measurements. Adsorption isotherms of water vapor onto two porous materials BC and IG-110 have been experimentally measured using the dynamic water vapor absorption instrument (DVS Adventure) at adsorption temperature 20°C. Experiments show that the moisture adsorption of IG-110 is much lower than that of BC at various relative humidity. The adsorption data is analyzed by various adsorption models which include BET, GAB, D-A, Oswin model. The GAB model gives the good fit for the relative humidity range of 0–0.95. The mean relative percentage deviation modulus is found 3.92 and 5.45 % for BC and IG-110, respectively.

![Figure 3. Fitting of experimental data for IG-110.](image)

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