

Study of Adsorption Dynamics for 5A Molecular Sieve Material in Manned Spacecraft

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Abstract—Air revitalization technology of environment control and life support system (ECLSS) should be developed for the long-time orbit mission of manned spacecraft. Two kinds of molecular sieve materials, TC-5A and PSA-5A, have made on request by China's manned space development demand, and the dynamic model of adsorbent bed in CO₂ removal subsystem is established. As the physical and the dynamics Parameters is known, the simulation shows the results as CO₂ concentration and temperature changes. The adsorbing experiment is established to verify the effectiveness of dynamic model, besides, it analyzed the adsorption performance in condition of different concentration and temperature. Study shows that established dynamic model of adsorption bed fit well with experiments and can reflect the adsorption process of two kinds of adsorption material. The modeling can be used as a part of the system simulation or system fault prediction and analysis in near future. In addition, temperature is the main factor of adsorption performance for two kinds of molecular sieves materials, the adsorption capacity sharply dropped as the adsorbing temperature rises. So the adsorbing temperature is the priority consideration when air revitalization system designed, so as to make sure the adsorbing is effective.

Keywords—manned spacecraft; 5A molecular sieve; dynamic modeling; adsorption performance; influence factor

I. INTRODUCTION

The astronaut is closely related to the spacecraft environment when executing assignment in space, which including cabin pressure, cosmic radiation, the micro-gravity environment, high and low temperature environment, harmful gases and trace pollutants, etc. In order to ensure the astronauts comfortable and safety

within the confined manned spacecraft, the environment control and life support system (ECLSS) should be developed^[1]. CO₂ removal technology research has always been focused on ECLSS of manned spacecraft, it has formed a comparatively accelerated CO₂ removal system after 40 years of development^[2]. In the short-term mission spacecraft, it usually use LiOH to remove CO₂, such as America's Mercury, Gemini, Apollo spacecraft^[3], Russian Soyuz spacecraft, China's Shenzhou spacecraft system. As for the long-duration space flight, as the Mir^[4], the Sky Lab, and the International Space Station (ISS), the regenerative adsorption system adopt 5A molecular sieve 13X Zeolite as the main CO₂ removal material.

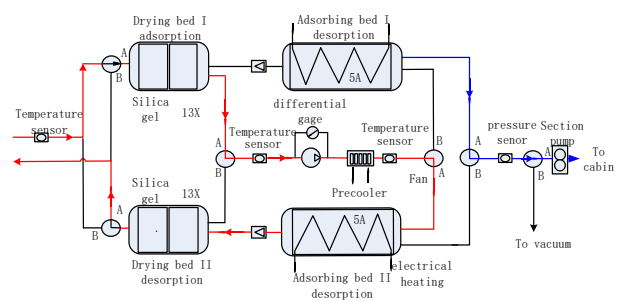


Figure 1. Flow diagram of 4-BMS adsorption/desorption

CO₂ adsorption and desorption techniques in ISS use four bed molecular sieves (4-BMS) system, which has advantage of material life and thermal stability, system reliability, security, materials research, as well as adsorption/desorption technology maturity et al^[5], and the 4-BMS system running performance still works quite well at present. Because of the development of molecular sieve

materials in China and the application fields expanding, it has qualified as the foundation of developing the molecular sieve material. Therefore, China selected 4-BMS CO₂ removal system as the key air revitalization technology of space station, 4-BMS CO₂ removal system adsorption/desorption process is shown in Fig. 1.

At present, a lot of CO₂ removal research applied to industrial applications, such as molecular sieve structure modification^[6], CO₂ adsorption performance in high temperature environment^[7], are all applied to the field of chemical industry in China. Foreign study of adsorbent are mainly includes 13X Zeolite^[8], activated carbon^[9], 4A Zeolite^[10], Active Aluminium^[11], Silica Gel^[12] et al. Study on the adsorbent adsorption performance of CO₂. According to the needs of the development of China's manned space flight, we developed two kinds of special molecular sieve materials, TC-5A and PSA-5A, which suitable for 4-BMS device^[13]. This article mainly study on molecular sieve adsorption performance both in experiment and simulation way, by simulating working condition of the molecular sieve adsorption, the process of dynamic simulation adsorbent bed can be evaluated in a convenient and fast mode, laying a foundation for system modeling and simulation, being beneficial to monitor working state of the ECLSS, and helping for fault diagnosis and decision support system (DSS).

II. DYNAMIC MODEL OF ADSORPTION BED

Dynamic model for adsorbent bed has been studied comparative perfect at home and abroad, Model of development has experienced from a single component adsorption to the multi-component adsorption, from isothermal, isobar adsorption to temperature and temperature swing adsorption, from ignoring the radial temperature and concentration changes gradually transferred to the continuous improvement of the actual adsorption process, finally get close to the real physical system of the mathematical model^[14]. To establish a mathematical model of adsorption bed, the following hypothesis are as follows^[15]:

- Adsorption process regard as an isothermal, component follows the linear isothermal adsorption equation;
- The gas velocity u considered as a constant in the process of adsorption;
- The heat and mass transfer are transient equilibrium, the mass transfer resistance in the process of adsorption described as linear driving force (LDF) equation;
- The flow in the tube hypothesis for plug flow, and ignoring the radial diffusion;
- The inlet gas treated as ideal gas, the axial pressure gradient along adsorption bed is ignored;

The gas phase diffusion mass balance including axial diffusion, convection, integral item and the source term in the adsorption process. According to the differential control of adsorption bed, equation established as follows:

$$-D_{zi} \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial}{\partial z} (u C_i) + \frac{\partial C_i}{\partial t} + \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \rho_p \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (1)$$

D_{zi} is axial diffusion coefficient, m²/s; C_i is CO₂ component concentration in gas phase, kg/m³; u is inlet gas velocity, m/s; z is length of adsorbent bed, m; ε_b is void ratio of the bed; \bar{q}_i is the molecular sieve average adsorption, kg/m³.

Adsorbent are homogeneous spherical particles, adsorbing process inside the particles described by Fick diffusion law:

$$\frac{\partial \bar{q}_i}{\partial t} = D_e \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right) = D_e \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial C_i}{\partial r} \right) \right) \quad (2)$$

Assuming that the concentration of the adsorbate on the adsorbent is parabolic distribution, the average adsorption quantity changes over time relationship can use LDF equation and Henry's law to solve^[15]:

$$\frac{\partial \bar{q}_i}{\partial t} = k_{bi} (q_i^* - \bar{q}_i) = k_{bi} K (c_i - c_i^*) \quad (3)$$

As $k_{bi} = \frac{15D_e}{R_p^2}$ is Mass transfer resistance coefficient,

1/s; K is Henry coefficient m³/kg.

Axial diffusion coefficient D_{zi} can be obtained by the following equation:

$$\frac{\varepsilon_b D_{zi}}{D_{mi}} = 20 + 0.5 \text{ScRe} \quad (4)$$

For the binary mixture under the condition of low pressure, D_{mi} can be used Chapman Enskog-formula :

$$D_{mi} = \frac{0.0018583 T^{2/3} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}}{P \delta_{AB}^2 \Omega(\varepsilon / KT)} \quad (5)$$

δ_{AB} is molecular collision diameter, m; Ω is Lennard-Jones Collision integral function, which is function of temperature ratio TK / ε (K is the Boltzmann constant, is molecular potential energy of interaction), δ_{AB} and $\Omega(TK / \varepsilon)$ can be found by literature, or the experience formula of literature.

The initial conditions are:

$$\bar{q}_i \Big|_{t=0} = 0; C_i \Big|_{z=0} = C_0, \quad t \geq 0$$

The boundary conditions are:

$$\frac{\partial C_i}{\partial z} \Big|_{z=L} = 0; \quad t \geq 0$$

III. MODEL VALIDATION AND EXPERIMENTAL ANALYSIS

The correctness and accuracy of the dynamic model should be verified with experiments, the influence of molecular sieve adsorption of CO₂ can be draw when the molecular sieve size, CO₂ concentration and adsorption temperature changed under different relative humidity (RH) environment.

A. The experimental device

Two kinds of manned space molecular sieve material, TC-5A and PSA-5A, applied in the experiment, which provided by the Zhengzhou fulong new material corporation. Gas source supplied by pure N₂ and CO₂ tank, and mixed through Mass Flow Controller, the flow rate is 1.5 L/min. adsorbing temperature is record when the mixed gas adsorbed. Besides, Heating Device can heat the tube to keep adsorption temperature stable, the CO₂ Infrared Analyzer can measure the outlet gas CO₂ concentration. The room temperature also measured by Temperature and Humidity Sensor. All the data measured record on a computer automatically through Data Acquisition Processing Unit, and the adsorption capacity measured by the High Precision Electronic Balance, the flow chart shown in Fig.2:

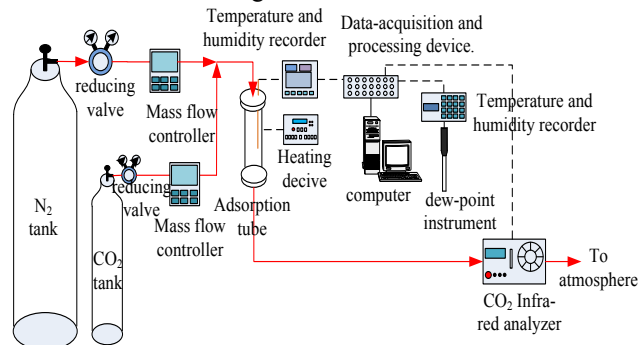


Figure 2. Flow diagram of the experiment for CO₂ adsorption of 5A molecular sieve

B. Adsorption bed model validation

Molecular sieve adsorption mathematical model contains partial differential equation, so the model should be discretization using numerical solution. Equation use forward difference in time, second-order central difference in space, and using first-order upwind difference scheme calculation. Combining with the experiment conditions, adsorbing related parameters shown in table 1:

TABLE I. SIMULATION PROCESS RELATED PARAMETERS

Adsorbent	TC-5A	TC-5A	TC-5A	TC-5A	PSA-5A	PSA-5A
Adsorbate	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂	CO ₂
Tem(°C)	25 °C	25 °C	25 °C	50 °C	25 °C	50 °C
K(m ³ /kg)	1.47	1.47	1.47	0.55	2.65	0.63
C ₀ (g/m ³)	8.98	12.57	17.96	12.57	12.57	12.57
k _{bi} (s ⁻¹)	0.007	0.007	0.007	0.02	0.080	0.11
ε _b	0.47	0.47	0.47	0.47	0.44	0.44
(kg/m ³)	900	900	900	900	950	950
Rp(mm)	1.000	1.000	1.000	1.000	0.375	0.375
L(m)	0.070	0.070	0.070	0.070	0.055	0.055
d(m)	0.02	0.02	0.02	0.02	0.02	0.02
u(m/s)	0.08	0.08	0.08	0.08	0.08	0.08

1) Experiment and simulation curve of TC-5A adsorption under room temperature

The inlet gas CO₂ concentration can be changed under experiment, and we can get the exit gas breakthrough

curve. The condition are the same when simulated, the results is shown in Fig.3:

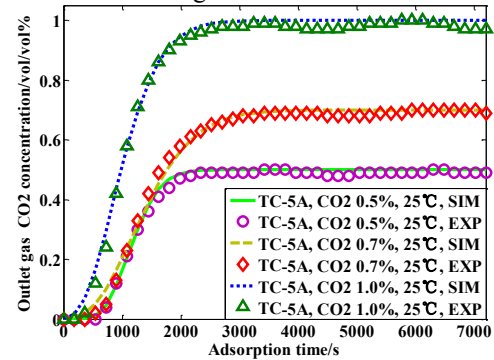


Figure 3. Experiment and simulation contrast curve of TC-5A CO₂ adsorption in room temperature

As can be seen from Fig.3: a) CO₂ breakthrough time of outlet gas in adsorption bed shorten with the increase of imported gas concentration, because the length of the bed only 7cm, the breakthrough time is just 3min around when the import CO₂ concentration is 1.0%. b) A certain amount heat of adsorption will be produced in adsorbing process, so the adsorption capacity in balance influenced when the temperature fluctuate, so as to the outlet gas CO₂ concentration. c) When the condition of simulation and experiment are identified, the curves of simulation are consistent with the experimental data, which shows that the dynamic model can well reflect the adsorbing process.

2) Experiment and simulation curve of TC-5A and PSA-5A adsorption under 50 °C

The adsorption bed is heated to 50 °C by the Heating Device, and the import gas CO₂ concentration is 0.7%, we test the TC-5A and PSA-5A export gas CO₂ concentration. Meanwhile, the simulation curve also got under the same initial condition of experiment, as Fig.4 shows. The adsorbing cure in room temperature added in the Fig.4 so as to better reflect the performance of adsorption influenced by temperature.

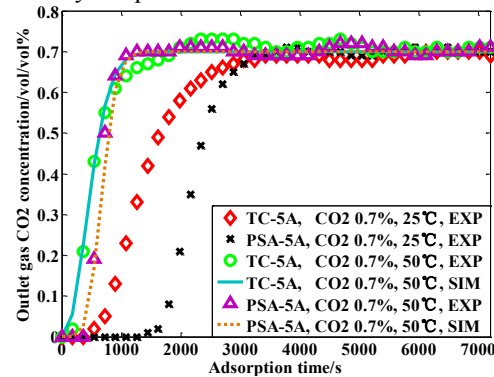


Figure 4. Experiment and simulation contrast curve of TC-5A and PSA-5A CO₂ adsorption in 50°C and room temperature

Fig.4 shows that: a) the breakthrough time shortens when the temperature rises, temperature is a key factor that affected the molecular sieve adsorption performance. b) The breakthrough time of PSA-5A is longer than TC-5A. When the temperature at 50 °C, the energy of the molecular sieve and the gas molecular rises, and the

absorption rates speed up, but the performance of PSA-5A is better than TC-5A. c) The overall mass transfer resistance coefficient k increases and the Henry coefficient k is reduced in the simulation parameter in 50°C, and the simulation curve obtained still has the very good agreement with the experimental results.

IV. CONCLUSION

Based on the aerospace development demands in China, this article established dynamic model of CO₂ adsorption in bed, which the molecular sieve material suitable for China's manned space mission, and using the numerical calculation method to obtain the breakthrough curve of adsorption bed under different environment. To test and verify the correctness and accuracy of model, the sample experiment is set up to get the verification, the conclusion are as follows:

1) According to the physical and kinetic parameters of the manned spacecraft molecular sieve, TC-5A and PSA-5A, two kinds of molecular sieve simulation curve obtained at room temperature and 50°C can be identify with the experimental results. The CO₂ adsorption dynamics model can simulate various concentrations within the adsorption bed under the process of adsorption, not only largely shortens the experiment time, reduce the investment, but can simulate all kinds of extreme conditions, which will be of great importance in fault diagnosis and decision support system (DSS), improve the real-time of flight control and security of system.

2) Compared with the TC-5A, the diameter of PSA-5A is smaller, which means that it has a larger specific surface area, the performance of the adsorption is better than TC-5A. The adsorption capacity can reach 3% under the condition of low concentration, which can meet the needs of the manned space regeneration adsorption. But PSA-5A will produce greater resistance in the adsorption bed, the energy consumption and investment will add with increasing the power of the fan. So the factor of volume, mass and energy consumption must be considered comprehensive when systems design.

3) Temperature is a key influence factor of molecular sieve adsorption performance. When temperature raised from room temperature (25 °C) to 50 °C, adsorption capacity of two molecular sieve materials dropped 60% around. So when the materials in adsorption cycle after desorption, the adsorption temperature should be cooled to the room temperature rapidly to ensure effective adsorption.

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