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Experimental study on cryogenic adsorption of methane by activated carbon for helium coolant purification of High-Temperature Gas-cooled Reactor

Hua Chang *, Zong-Xin Wu, Hai-Jun Jia

Key Laboratory of Advanced Reactor Engineering and Safety of Ministry of Education, Collaborative Innovation Center of Advanced Nuclear Energy Technology, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China

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ABSTRACT

The cryogenic adsorption behavior of methane on activated carbon was investigated for helium coolant purification of high-temperature gas-cooled reactor by using dynamic column breakthrough method. With helium as carrier gas, experiments were performed at −196 °C and low methane partial pressure range of 0–120 Pa. The breakthrough curves at different superficial velocities and different feed concentrations were measured and analyzed by the mass-transfer zone model. The methane single-component adsorption isotherm was obtained and fitted well by the Toth model and the Dubinin-Radushkevich model. The adsorption heat of methane on activated carbon was estimated. The cryogenic adsorption process of methane on activated carbon has been verified to be effective for helium coolant purification of high-temperature gas-cooled reactor.

1. Introduction

The adsorption process is usually used for purification of industrial gas and also applied to helium coolant purification of high-temperature gas-cooled reactor (HTGR) (Olson et al., 1980; Sakaba et al., 2004; Yao et al., 2002; Chang and Wu, 2009; Chang et al., 2015). To avoid oxidation of graphite and corrosion of reactor structural materials, helium purification system as an indispensable auxiliary system of HTGR is set up to eliminate various gaseous impurities entering primary circuit coolant to limited levels. These impurities include chemical components such as hydrogen, water vapor, oxygen, carbon monoxide, carbon dioxide, methane and nitrogen as well as radionuclide fission products such as krypton and xenon etc. According to present design of HTGR, helium purification system generally consists in sequence of particulate filter for removing dust in primary circuit and three fixed-beds, that is, copper oxide bed, molecular sieve adsorber and cryogenic activated carbon adsorber. The copper oxide bed firstly converts hydrogen (including trace of tritium) and carbon monoxide to more easily adsorbed components of water (tritium to tritium water) and carbon dioxide, and simultaneously removes oxygen. Then the molecular sieve adsorber adsorbs carbon dioxide and tritium-containing water vapor. Finally, the cryogenic activated carbon adsorber immersed in liquid nitrogen bath removes the residual gas impurities such as methane and nitrogen as well as radionuclide krypton and xenon (Liao et al., 1995, 1998, 2001). Helium purification system in essence uses microporous adsorbents such as molecular sieve and activated carbon to remove traces of gas impurities from primary circuit coolant to ensure safe operation of HTGR.

At present, a demonstration plant of high-temperature gas-cooled reactor-pebble bed module (HTR-PM), based on the technology of the 10 MW High-Temperature Gas-cooled Reactor-test module (HTR-10), is under construction and will be put into operation in about 2017 in China (Zhang et al., 2009). The obtainment of adsorption data for various impurities on corresponding adsorbents is fundamental and critical for the design and operation of helium purification system of high-temperature gas-cooled reactor. However, there still lacks essential equilibrium and kinetic data to be used for the design of cryogenic activated carbon adsorber. To optimize the process design and operation, this paper mainly focuses on the investigation of cryogenic adsorption capability of methane on activated carbon for helium coolant purification of HTGR. The operation pressure of HTR-PM is 7 MPa and methane concentration is typically about 3 ppm, so the methane operation partial pressure is about 21 Pa. In the past, a number of researches of methane adsorption on various activated carbon have been extensively made at assorted pressures and temperatures for either natural gas storage or methane separation,

* Corresponding author. Tel.: +86 10 89796048; fax: +86 10 69771464.
E-mail address: changhua@mail.tsinghua.edu.cn (H. Chang).

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Nomenclature

A	adsorption potential, J·mol^{-1}
b	adsorption equilibrium constant in the Toth model, Pa^{-1}
C_i	feed concentration of methane
C_o	outlet concentration of methane
E	characteristic energy in the D-R model, J·mol^{-1}
E_0	characteristic energy towards a reference adsorbate, J·mol^{-1}
j	the number of data point used for model fitting
L_B	fixed-bed length, mm
LES	length of equilibrium section in the MTZ model, mm
LUB	length of unused section in the MTZ model, mm
m	mass of adsorbent packed in the adsorber, g
M	molecular weight of methane, g·mol^{-1}
P_i^s	vapor pressure of adsorbate at adsorption temperature, Pa
P_i	partial pressure of adsorbate, Pa
q^{exp}	experimental value of adsorption equilibrium data, g/100 g adsorbent
q^{cal}	model predicting value of adsorption equilibrium data, g/100 g adsorbent
q	equilibrium adsorption capacity of methane, g/100 g adsorbent
q_m	maximum adsorption capacity in the Toth model, g/100 g adsorbent
q'	kinetic adsorption capacity of methane at breakthrough point, g/100 g adsorbent
R	gas constant, 8.314 J·mol^{-1}·K^{-1}
R^2	deviation square
t	temperature-dependent adsorption constant in the Toth model
t_b	breakthrough time, min
t_s	mean residence time, min
t_∞	run time which is long enough to reach equilibrium with the feed concentration, min
T	adsorption temperature, K
V_s	volumetric flow rate of feed gas at standard condition (0 °C and 101 kPa), L·min^{-1}
W_0	the limiting micropore volume, cm^3·g^{-1}
W	the volume adsorbed, cm^3·g^{-1}
ΔH_{ads}	isosteric adsorption heat, J·mol^{-1}
Δq	maximum relative deviation of equilibrium adsorption capacity for model fitting

Greek letters

β	affinity coefficient in the D-R model

which put their emphasis on high pressure adsorption for the application of pressure swing adsorption technology (Luo et al., 2011; Choi et al., 2003; Al-Muhtaseb, 2010; Rufford et al., 2013). However, the comprehensive adsorption data of methane on activated carbon at low partial pressure range and cryogenic adsorption condition serving for helium coolant purification have been scarcely reported in open literature.

To provide reliable adsorption data and experimental verification of cryogenic activated carbon adsorption for helium coolant purification, the adsorption capability of methane on activated carbon was investigated by using dynamic column breakthrough method. A pilot-scale fixed-bed adsorber was designed to perform cryogenic adsorption experiments at low partial pressure with helium as carrier gas. A commercial coconut shell activated carbon used in helium purification system of both the HTR-PM and the HTR-10, was selected as the adsorbent in this work. Experiments were conducted at near atmosphere pressure by keeping the same methane partial pressure as helium purification system of HTGR. The experimental breakthrough curves at different operation conditions were analyzed by the mass-transfer zone model and the effects of superficial velocity and feed concentration on adsorption capability were discussed. The adsorption isotherm of methane on activated carbon was determined and fitted by two adsorption equilibrium models. The data obtained can be used in designing, sizing and operating the cryogenic activated carbon adsorption process more efficiently for helium coolant purification of HTGR.

2. Materials and methods

2.1. Materials

The adsorbent used is a commercial coconut shell steam-activated carbon in the form of amorphous granule of 10–16 mesh, supplied by Shanghai XingChang activated carbon Co., Ltd. (China). The physical properties are tabulated in Table 1. The pore structural characteristics of the activated carbon were determined by N_2 adsorption at 77 K using a commercial ASAP2020 apparatus (Micromeritics, USA). The activated carbon was degassed at 573 K with vacuum to 1 μmHg for more than 8 h to remove impurities. The N_2 isotherm at 77 K and the pore size distributions (PSD) calculated using the nonlocal density functional theory method of N_2-DFT model with slit geometry in Micromeritics software are shown in Fig. 1. The fact that N_2 adsorption isotherm at 77 K is highly favorable at low partial pressure indicates the adsorbent has a large volume of micropores, which conforms to the micropore filling mechanism. The essential coincidence between the adsorption and desorption isotherms suggests that the activated carbon only contains a little small volume of mesopores. The cumulative pore volume and pore size distribution also show that the activated carbon includes a large volume of micropores with widths in the range of 5–20 Å.

Table 1
Properties of the coconut shell activated carbon.

Properties	Activated carbon
Particle size(mesh)	10–16
Bulk density(kg·m^{-3})	493
BET surface area(m^2·g^{-1})	914
Total pore volume(cm^3·g^{-1})	0.44
Micropore volume(cm^3·g^{-1})	0.36

Pure gases of helium and methane used were supplied by Beijing AP BAIF Gases Industry Co., Ltd. (China), with the purity at a grade of 99.999% and 99.995%, respectively. The activated carbon was regenerated by purging pure helium of 150 °C for at least 3 h, then taken out the adsorber and quickly weighed. The activated carbon was reloaded subsequently and used iteratively in the experiments. The weight of the activated carbon packed is 24.201 g, which is measured by an electrical scale with the precision of ±0.001 g.

2.2. Experimental set-up and procedures

The experimental apparatus is shown schematically in Fig. 2. Based on our previous work for carbon dioxide adsorption on molecular sieve (Chang and Wu, 2009), the apparatus had been improved to meet cryogenic methane adsorption on activated