Investigation of breakthrough curve of 10K cryogenic adsorber in helium refrigerator

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Abstract. High pure quality helium is required in helium refrigerator and cryogenic adsorber is essential in cryogenic engineering system, while there is a lack of cryogenic adsorption data below 20K which causes inconvenience when it comes to the design of cryogenic adsorber. The paper mainly deals with the design of a 10K cryogenic adsorber in a helium refrigerator which works at 250W@4.5K. Isothermal and nonlinear dispersion plug flow model is built to investigate the breakthrough curve of trace hydrogen with helium being the carrier gas. It can help in lateral design of cryogenic adsorber.

1. Introduction

With the development of experimental science and Particle physics, Helium refrigerator is the only solution to the realization of stable ultimate low temperature environment. High pure quality helium is required in helium refrigerator and cryogenic adsorber is essential in cryogenic engineering system. The design of the cryogenic adsorber is usually based on the static adsorption capacity of gases adsorbed on porous material; such as coconut based activated carbon, zeolite, and carbon molecular sieve; Kidnay and Hiza\cite{1} has summarized the physical adsorption data in cryogenic engineering, including the pure component and gas mixture isotherms; Adsorption kinetics are also discussed, the method of Eagleton and Bliss is assumed preferable in evaluation of the mass transfer coefficient\cite{1, 2}. Johannes\cite{3} has found that the presence of helium has little effect on nitrogen adsorption; Ruthven and Farooq\cite{4} studied the trace component by pressure swing adsorption and found that hydrogen and helium are adsorbed non-competitively, the presence of high pressure helium doesn’t impede the adsorption of hydrogen; more experimental data is needed to test the effect of helium presence on gas adsorption in more binary and ternary systems; Although there’re already many cryo-sorption data available in literatures, they’re not available in the desired temperature or pressure regime in most cases\cite{1}, the potential theory given by Polynyi\cite{1, 5} and the ideal adsorbed solution theory proposed
by Myers and Prausnitz[6] are useful tools to predict pure component and gas mixture adsorption respectively.

In cryogenic engineering, the adsorption in packed bed is actually a dynamic process. Due to the resistance of heat and mass transfer, the adsorption process cannot reach equilibrium once the impure gas reaches the surface of the adsorbent. As a result, the dynamic adsorption capacity is usually smaller than the static one for single pass depending on the flow rate and column dimension. With the semi-empirical process design of the cryogenic adsorber based on the static adsorption capacity, experimental or theoretical analysis on the operating process of the purifier must be done for sake of the safe operation of the system. Breakthrough curve is a good way to study the propagation of the adsorption front and gives us the exact time that the adsorber is still effective.

The motif of this study is to investigate the breakthrough curve of a 10K cryogenic adsorber in helium refrigerator which works at 250W@4.5K, using the partial differential equations regarding the heat and mass balance, the breakthrough time or the life cycle of the adsorber is obtained which is helpful in lateral design of the cryogenic adsorber.

2. Design of the cryogenic adsorber
There’s a helium refrigerator being built by the Technical Institute of Physics and Chemistry, Chinese Academy of Science, which works at 250W@4.5K with helium liquefaction, it’s showed in Figure 1. It’s a typical helium Brayton cryo-refrigerator cycle in large scale cryogenic engineering[7]. Because of the liquefaction, crude helium should be replenished to the system constantly as make-up to the pressure drop. The impure gas in the crude helium can be condensed and solidified under low temperature so as to plug the system, and even bring damage to the turbine expander[8], thus the accurate design of the helium purifier is essential. In the 250W@4.5K helium refrigerator, there’s a cryogenic adsorber which lays at the outlet of the five-stage heat exchanger works at 10K to remove hydrogen and neon. Working condition is showed in Table 1. The resupplied gas is bottled pure helium conforming National Standard of the People’s Republic of China, concentration of impure gas can be seen from Table 2. Most of the impure gas was solidified and removed at 10K except the neon and hydrogen. From Table 3, it can be seen that hydrogen and neon are both below the triple point temperature at 10K. Considering the gas-solid saturation vapour pressure, the gas-solid saturation vapour pressure of neon is much smaller than that of hydrogen and thus can be neglected in the calculation; therefore hydrogen is considered to be the only gas needed to be removed from the crude helium.

![Schematic diagram of the helium refrigerator which works at 250W@4.5K](image-url)
Table 1 Operating Parameters of the cryogenic adsorber

| Para. | $T_{in}$/K | $P_{in}$/Bara | $\dot{m}_1$/g \cdot s$^{-1}$ | $\dot{m}_2$/ g \cdot s$^{-1}$ | $\Delta P$/Pa |
|-------|------------|---------------|-------------------------------|-------------------------------|-------------|
| value | 10         | 9.97          | 22.4                          | 3.282                         | 500         |

Table 2 Component in Bottled helium confirming National Standard of the People’s Republic of China

| Gas     | $T_{pr}$/K | $T_{bc}$/K | $T_{e}$/K | $P_0$/Pa |
|---------|------------|------------|-----------|-----------|
| Neon    | 24.556     | 27.104     | 44.492    | 0.00805   |
| Hydrogen| 13.957     | 20.369     | 33.145    | 235.87    |

2.1. Cryogenic adsorption data

In order to design the adsorber, gas adsorption data is needed. Lack of hydrogen adsorption data at 10K, it’s impossible to design the adsorber accurately, while the adsorption potential theory is a good way to solve the problem. The adsorption potential theory developed by Dubinin[9] ascribes adsorption to the dispersion force which is independent of temperature between molecules, a characteristic curve can be obtained which could be used to evaluate the adsorption equilibrium data using only single experimental adsorption isotherm[10]. The adsorption data of hydrogen at 10K has been calculated using the adsorption data of hydrogen at 22K, 27K, 32K, and 37K on charcoal from Yamk et al[11, 12] with the potential theory. It can be seen from Figure 2. Because helium is the majority of the gas mixture, the competitive adsorption of helium and hydrogen should be evaluated. Helium adsorption data comes from Krishnamoorthy et al[13] and correlated by the multilayer adsorption model built by zou et al[14], it’s showed in Figure 3. The adsorption capacity of hydrogen at 7ppm and helium at 9.97bara on charcoal at 10K is 0.556m$^3$/g and 0.95$\times$10$^{-3}$ m$^3$/g respectively. Therefore, the competitive adsorption of helium over hydrogen on charcoal can be neglected.

Fig. 2 Adsorption of hydrogen on charcoal at 10K  
Fig. 3 Adsorption of helium on charcoal at 10K
In large scale cryogenic engineering system, there should be no more than 50ppm impurities in the crude helium, otherwise it may cause gas solidification and bring damage to the moving parts in the system. For the 250W@4.5K helium refrigerator being built by the Technical Institute of Physics and Chemistry, Chinese Academy of Science, there’s refrigeration mode and helium liquefaction mode. During the liquefaction mode, crude helium should be resupplied constantly. We use bottled pure helium conforming National Standard GBT 4844-2011 of the People’s Republic of China as displayed in Table 2. The resupplied gas is first precooled by the main flow and then flows into the adsorber. From the previous discussion, we know that the gas mixture entering the adsorber is assumed to be hydrogen-helium binary system, the concentration of hydrogen is 7ppm in the crude helium, the total inlet gas pressure is 9.97bara, temperature is 10K, and resupplied gas flow rate is 3.282g/s. In order to evaluate the numerical model, the resupplied gas flow rate is used other than the total flow rate to design the adsorber. With all these data, the cryogenic adsorber is designed; because the motif of the paper is to investigate the adsorption dynamics, the design process can be found in the paper[12]. The adsorbent is granular activated carbon, packed bed density is 514kg/m³, bed porosity is 0.4; the depth of the adsorption column is 20cm, the inner diameter of the column is 6.8cm. 

Table 4 Parameters of the cryogenic adsorber which works at 250W@4.5K

| Parameter | Value |
|-----------|-------|
| ε         | 0.4   |
| ρₙ / kg · m⁻³ | 514   |
| dₚ / m    | 0.002 |
| m / kg · m⁻³ | 9.927 |
| H / m     | 0.2   |
| d / m     | 0.068 |
| H/d ratio | 3     |

2.2. Investigation of adsorption dynamics

Zhang et al [15, 16] have built a model for the isothermal operation of a packed bed adsorption process with hydrogen transported at low mole fraction by an inert carrier gas, towards the adsorption dynamics of a helium purifier. Because the fraction of hydrogen is so small that the adsorption heat of hydrogen on activated carbon can be neglected. So the adsorption process is assumed to be isothermal. Other assumptions are: neglect of velocity variation, adsorption equilibrium is reached instantly, with conservation of mass, the following model is derived:

$$-D_L \frac{\partial^2 C_i}{\partial z^2} + u \frac{\partial C_i}{\partial z} + \frac{\partial C_i}{\partial t} + \frac{1 - \varepsilon_b}{\varepsilon_b} \rho_p \frac{\partial q_i}{\partial t} = 0$$ (1)

Where $D_L$ is the axial dispersion coefficient, it can be calculated by the following equations[17]:

$$D_L = 0.73 D_w + 0.5 \frac{ud_p}{1 + 9.7 D_M / ud_p}$$ (2)

$D_m$ is the molecular diffusivity which can be calculated by Suzuki[18]:

$$D_L = \frac{0.001858T^{\frac{3}{2}}}{\rho_0 \sigma_{AB}^2 \Omega_{AB}} \left[ \left( \frac{M_A + M_B}{M_A M_B} \right)^{\frac{1}{2}} \right]$$ (3)
With the law of conservation of mass, the boundary condition is:

\[ z = 0 : \quad D_t \frac{\partial C_i}{\partial z} = -v \left( C_i \bigg|_{z=0} - C_i \bigg|_{z=0} \right) \quad (4) \]

\[ z = L : \quad \frac{\partial C_i}{\partial z} = 0 \quad (5) \]

Initial condition is:

\[ C_i(z,0) = 0; q_i(z,0) = 0 ; \quad (6) \]

\[ C_i(0,t) = c_{i,in}; q_i(0,t) = q_{i,in} \quad (7) \]

As showed by Ruthven[19], during the adsorption process of trace hydrogen from helium carrier gas, the axial mass transfer can be negligible, the differential mass balance in the packed bed can be simplified to this:

\[ \frac{u \frac{\partial C_i}{\partial z} + \frac{\partial C_i}{\partial t} \frac{1 - \epsilon_p}{\epsilon_p} \rho_p \frac{\partial q_i}{\partial t}}{\epsilon_p} = 0 \quad (8) \]

3. Results and discussions

The average Isosteric heat of adsorption for hydrogen adsorbed on charcoal is 3.6kJ/mol[11], we did some calculations and found that the temperature rise of the crude helium due to hydrogen adsorption heat is about 0.002K. So in the numerical simulation, the thermal effect of adsorption is neglected and the heat balance equation is not within our consideration. With the equilibrium adsorption data, the breakthrough curve is obtained through resolving Eqs(1)-(8); The axial dispersion term uses the explicit central difference; Other terms use the backward difference; The breakthrough curve with or without dispersion term is showed in Figure 4. From Figure 4, we can see that the breakthrough time of the adsorber is about 83h with or without axial dispersion; The axial dispersion speed up the breakthrough process and makes the adsorber lose its effectiveness more easily. The breakthrough curve is sharper for the ideal process neglecting dispersion effect as the read solid line displayed in Figure 4; and the trace hydrogen appears at the outlet of the adsorber several hours later compared to that of the real dynamic adsorption process.
From Eq.(8), we can get the propagation velocity of the mass transfer front[16]:

\[
w_c = \left( \frac{\partial z}{\partial t} \right)_c = -\left( \frac{\partial C}{\partial t} \right)_c = \frac{u}{1 + \left( 1 - \frac{\varepsilon_b}{\varepsilon_b} \right) \rho_p \left( \frac{dq}{dC} \right)}
\]  

(9)

The mean retention time is:

\[
\bar{t} = \frac{H}{w_c}
\]

(10)

The superficial velocity is 0.015 m/s, the adsorption isotherm of hydrogen on charcoal at 10K can be found by[12], the relationship of gas pressure and molar concentration can be derived from the gas equation of state; Through Eq.(9) and (10), the wave propagation velocity is 1.41x10^-7 m/s, the retention time is 395h; It’s far deviated from the breakthrough time, as we know, because of the resistance of heat and mass transfer, the assumption of constant local equilibrium on the adsorbent surface is imperfect. The breakthrough time could be much shorter and the purifier should be regenerated more frequently. The model is simple and more theoretical and experimental work should be done in the near future.

**Conclusions**

Cryogenic adsorber is an essential facility for helium purification in large scale cryogenic engineering. In order to investigate the adsorption dynamics of the 10K cryogenic adsorber in the 450W@4.5K helium refrigerator, an isothermal, nonlinear plug flow is introduced to investigate the breakthrough curve; it shows that the existence of axial dispersion speeds up the breakthrough process and shortens
the elapsed time of the adsorber. More complex adsorption dynamic model still needs to be built, accurate experimental adsorption data of helium and hydrogen on specific adsorbent is still needed to help design of cryogenic adsorber.

Nomenclature

\[ \begin{align*}
C & \quad \text{Gas concentration} \quad \text{mol} / \text{m}^3 \\
\theta & \quad \text{Diameter} \quad \text{m} \\
D_L & \quad \text{Axial dispersion coefficient} \quad \text{m}^2 / \text{s} \\
D_m & \quad \text{molecular diffusion diffusivity} \quad \text{m}^2 / \text{s} \\
H & \quad \text{Adsorbent Height} \quad \text{m} \\
m & \quad \text{Adsorbent quantity} \quad \text{kg} \\
M & \quad \text{Species molecular weight} \quad \text{g} / \text{mol} \\
m_s & \quad \text{Resupplied crude helium flow rate} \quad \text{kg} / \text{s} \\
m_t & \quad \text{Total Gas flow rate} \quad \text{kg} / \text{s} \\
P_0 & \quad \text{Saturated vapour Pressure at 10K} \quad \text{Pa} \\
P_{in} & \quad \text{Gas inlet pressure of the adsorber} \quad \text{Pa} \\
\Delta P & \quad \text{Allowed max Pressure Drop} \quad \text{Pa} \\
q & \quad \text{Local equilibrium adsorption} \quad \text{mol} / \text{g} \\
T_b & \quad \text{Normal boiling point temperature} \quad \text{K} \\
T_c & \quad \text{Critical temperature} \quad \text{K} \\
T_{in} & \quad \text{Gas inlet temperature of the adsorber} \quad \text{K} \\
\Omega & \quad \text{Triple point Temperature} \quad \text{K} \\
u & \quad \text{Interstitial velocity, which equals to } v / \varepsilon \quad \text{m} / \text{s} \\
w & \quad \text{Wave propagation velocity} \quad \text{m} / \text{s} \\
\varepsilon & \quad \text{Packed bed porosity} \\
\rho & \quad \text{Density} \quad \text{kg} / \text{m}^3 \\
v & \quad \text{Superficial velocity of fluid} \quad \text{m} / \text{s} \\
\sigma_{AB} & \quad \text{Collision integral, a function of } k_{AB}T / \varepsilon_{AB} \text{ where } k_{AB} \text{ is the Boltzman's constant} \\
\Omega_{AB} & \quad \text{Lennard-Jones constant} \\
A & \quad \text{Helium} \\
B & \quad \text{Hydrogen} \\
b & \quad \text{Packed bed} \\
f & \quad \text{fluid} \\
i & \quad \text{The ith component} \\
in & \quad \text{Inlet} \\
p & \quad \text{Adsorbent Particle}
\end{align*} \]
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