Mathematical model of gas mixture adsorption by a composite adsorbent

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Abstract. Within a framework of mechanics of multiphase media a mathematical model of the dynamics of a helium and water vapor mixture flowing through a bed of composite adsorbent, based on microspheres and aluminum oxide, is derived. It is shown how to coincide the flow in porous media of adsorber and gas diffusion in a cylindrical granule of adsorbent taking into account helium adsorption by microspheres and water vapor by a porous surface of an adsorbent.

1. Introduction

Nowadays, natural gas is the only practical source of helium, and the predominant technology of helium extraction is cryogenic, which is expensive, material- and energy-consuming, and is effective only for large amounts of raw material treatment. Alternative technologies, such as membrane and absorption, are practically isolated from industrial facilities, because they cannot provide the required capacity.

Exclusively high helium selectivity of quartz membranes is known for quite a long time. The permeability factor of quartz glass for helium exceeds one for methane by seven orders ($L_{He} = 3.26 \cdot 10^{-15}$ mole/(m\textsuperscript{2} s Pa); $L_{CH_{4}} = 6.38 \cdot 10^{-22}$ mole/(m\textsuperscript{2} s Pa)). However, utilization of quartz or other silicate materials such as common flat or capillary-tube membranes is difficult because of the low rate of helium diffusion, complicated organization of a large mass-transfer surface, and membrane performance at high pressure difference on both membrane sides.

The authors proposed the pioneering approach for the creation of the materials selectively absorbing helium; the approach combines the membrane and sorption technologies. It is suggested that hollow glass microspheres be used as membrane elements. Due to the selective permeability of some glasses, helium diffuses into the microsphere cavity because of the difference of partial pressures of helium inside and outside the microsphere. The method is referred to as the membrane-sorption, because the microsphere shell is a membrane, and the particle itself (the microsphere) absorbs helium inside. The particle sizes enable to create the large mass-transfer surface, whereas the spherical shape provide high hydrostatic strength. The presence of many micron-size particles guarantee the large surface of the mass transfer.

The composite absorbent is created in cooperation with the Institute of Problems of Hydrocarbons Treatment SB RAS, Omsk. Synthetic glass microspheres are used as the helium-
Figure 1. Structured levels of flow design: 1 – free adsorber volume; 2’ – adsorber volume occupied by cylindrical granules; 2 – free space inside a granule; 3 – volume occupied by microspheres in a granule; 4 – porous binder volume in a granule.

permeable component of the composite adsorbent, and aluminum hydroxide (pseudoboehmhte) works as a binder. The composite absorbent binder has a developed porosity and a big specific surface which is widely used as an absorbent for drying various gases and liquid media. Microsphere granulation into cylindrical granules from pseudoboehmite permits solving several tasks simultaneously: first, to reach the optimal granule size for feeding into an industrial absorber, second, to realize simultaneous helium occlusion and water removal from the gas mixture [1].

Gas flow through an adsorbent consists of gas filtration through the cylindrical granules, diffusion inside these granules, water vapor adsorption on a binder and helium adsorption by microspheres figure 1.

This kind of flow is described by models with double porosity with filtration through a free volume of adsorber and through a free volume of a granule. Porous structure of an absorbent is mostly consists of mesopores with character channel diameter up to 200 nm. This fact makes the Knudsen diffusion mechanism be a driving force of flow inside the granule.

2. Mass transfer in adsorber
Suppose isothermic gas mixture flow of helium and water vapor through a bed of cylindrical granules evenly distributed in space. Mass conservation laws are averaged in investigated areas (figure 1) [2] using the method of volume averaging [3] and the interpenetrating continuum method [4]. Consider a "large" macro-volume \( \omega \) in a neighborhood of a chosen point \( \xi \) in the adsorber region. Consider \( \omega_1 \) to be a free volume, \( \omega'_2 \) – cylindrical granules volume, \( s_{12} \) – granules surface inside \( \omega \). Consider volume concentrations \( m_1, m_2 \) and a unit surface \( \alpha_{12} \) defined by

\[
m_1 = \omega_1 / \omega, \quad m_2 = \omega'_2 / \omega, \quad \alpha_{12} = s_{12} / \omega.
\]

(1)

From geometric considerations it is easy to establish the following relations between the parameters

\[
m_2 = 1 - m_1 = kV_p / \omega, \quad \alpha_{12} = kS_p / \omega,
\]

(2)

\[
V_p = \pi d_p^2 L_p / 4, \quad S_p = \pi d_p (d_p / 2 + L),
\]

where \( V_p, S_p \) – volume and surface of a cylindrical granule of length \( L_p \) and diameter \( d_p \); \( k \) – granules quantity in \( \omega \).
Further parameters \(m_1, k, \alpha_{12}, L, d\) are considered to be constant.

Local density of each component dynamics in a free volume of adsorber is described by the following equations with boundary conditions

\[
\frac{\partial \rho_{1i}}{\partial t} + \text{div} \, \rho_{1i} \mathbf{v}_1 = 0, \tag{3}
\]

\[
\rho_{1i} \mathbf{v}_1 \cdot \mathbf{n}|_{\Gamma_{12}} = -D_i \nabla \rho_{2i} \cdot \mathbf{n}|_{\Gamma_{12}} \quad (i = 1, 2),
\]

where \(\rho_{1i}, \rho_{2i}\) – local density of helium and water vapor in a free volume of adsorber and free volume of granules \((i = 1, 2)\); \(\mathbf{v}_1\) – local gas mixture components velocity in adsorber; \(\Gamma_{12}\) – interphase surface in adsorber; \(\mathbf{n}\) – outer unit normal vector to surface \(\Gamma_{12}\); \(D_i\) – Knudsen diffusion coefficient of the \(i\)th phase. The last condition in (3) expresses the fact that mass flux on the surface of a cylindrical granule equals to the diffusion flux out of or into the granule.

After averaging equations (3) with boundary conditions one has

\[
\frac{\partial \langle \rho_{1i} \rangle^1}{\partial t} + \text{div} \, \langle \rho_{1i} \mathbf{v}_1 \rangle^1 = -\alpha_{12} \langle \rho_{1i} \mathbf{v}_1 \cdot \mathbf{n} \rangle_{s_{12}} \quad (i = 1, 2), \tag{4}
\]

here

\[
\langle \varphi(t, \mathbf{x}) \rangle_i(t, \xi) = \frac{1}{\omega_i(\xi)} \int_{\omega_i(\xi)} \varphi(t, \mathbf{x}) d\mathbf{x}, \quad \langle \varphi(t, \mathbf{x}) \rangle_i^1(t, \xi) = \frac{1}{\omega} \int_{\omega(\xi)} \varphi(t, \mathbf{x}) d\mathbf{x}, \tag{5}
\]

\[
\langle \varphi(t, \mathbf{x}) \rangle_{s_{ij}}(t, \xi) = \frac{1}{s_{ij}(\xi)} \int_{s_{ij}(\xi)} \varphi(t, \mathbf{x}) d\mathbf{x}, \tag{6}
\]

where \(\varphi(t, \mathbf{x})\) – scalar, vector or tensor function, defined in an investigated area \(\omega_i\) and on an interphase boundary surface \(s_{ij}\) of \(i\)th and \(j\)th phase.

Neglecting the fluctuations of \(\rho_{1i}\) and \(\mathbf{v}_1\) in \(\omega_1\) one gets

\[
\langle \rho_{1i} \mathbf{v}_1 \rangle^1 \approx \langle \rho_{1i} \rangle^1 \langle \mathbf{v}_1 \rangle^1, \tag{7}
\]

and the right hand side of (4) using the boundary condition can be estimated as

\[
\alpha_{12} \langle \rho_{1i} \mathbf{v}_1 \cdot \mathbf{n} \rangle_{s_{12}} \approx -k/\omega \int_{S_g} D_i \nabla \rho_{2i} \cdot \mathbf{n} dS, \tag{8}
\]

where \(S_g\) – surface of a chosen granule, characterizing a state of all granules inside \(\omega\).

3. Mass transfer in granule

Consider gas diffusion inside cylindrical particle considering mass transfer with the free space of adsorber and interaction with inner structure of granule (helium permeation in microspheres and water vapor adsorption on binder surface).

Diffusion of local density in granule in volume 2 (figure 1) is described by the equation

\[
\frac{\partial \rho_{2i}}{\partial t} = D_i \Delta \rho_{2i} \quad (i = 1, 2). \tag{9}
\]

Consider the following boundary conditions for helium and water vapor

\[
\rho_{2i}|_{\Gamma_{12}} = \rho_{1i}|_{\Gamma_{12}}, \quad -D_i \nabla \rho_{2i} \cdot \mathbf{n}|_{\Gamma_{23}} = \frac{C_m \beta}{d} (\langle p_{31} \rangle_3 - \langle p_{21} \rangle_2), \quad -D_i \nabla \rho_{2i} \cdot \mathbf{n}|_{\Gamma_{24}} = 0, \tag{10}
\]
where $\Gamma_{12}$ – boundary between inner free space of a granule and a free space of adsorber; $\Gamma_{23}$ – microsphere surface inside granule; $\Gamma_{31}$ – surface of porons binder inside granule; $C_m$ – permeability coefficient of microsphere shell; $r$, $R$, $d$ – cavity radius, radius, shell thickness of microsphere; $\langle p_{31} \rangle_3$, $\langle p_{21} \rangle_2$ – averaged value of pressure inside and outside the microspheres in the neighborhood of a chosen point defined by (5).

The first condition implies the equality of local density for helium on the surface boundary, the second condition – mass flux in and out of microspheres is proportional to the difference of partial averaged pressure of helium inside and outside the microsphere; the third – helium is not adsorbed by a binder.

Helium adsorbed by microspheres is accounted by the following law

$$\frac{\partial}{\partial t}(V_m \rho_{31}) = -\frac{C_m S_m \beta}{d} \left(\langle p_{31} \rangle_3 - \langle p_{21} \rangle_2\right),$$

where $\rho_{31}$ – local helium density in a chosen microsphere; $V_m = 4/3\pi r^3$ – microsphere cavity volume; $S_m = 4\pi R^2$ – microsphere surface area.

Local helium pressure in $\omega_2$ and $\omega_{31}$ is defined by

$$p_{21} = \rho_{21} R_1 T, \quad p_{31} = \rho_{31} R_1 T,$$

where $T$ – temperature; $R_1$ – helium gas constant.

For water vapor boundary conditions are

$$\rho_{22}|_{\Gamma_{12}} = \rho_{12}|_{\Gamma_{12}}, \quad -D_2 \nabla \rho_{22} \cdot n|_{\Gamma_{23}} = 0, \quad -D_2 \nabla \rho_{22} \cdot n|_{\Gamma_{24}} = \beta_w (\langle \rho_{42} \rangle_{s_{24}} - a(\langle p_{22} \rangle_2, T)), \quad (12)$$

where $\beta_w$ – equilibrium adsorption rate of water vapor; $\langle p_{22} \rangle_2$ – averaged value of local water vapor density in the neighborhood of a certain point defined by (5); $a = a(\rho, T)$ – adsorption isotherm; $T$ – temperature.

The first condition implies the equality of local density for water vapor on the surface boundary, the second – water vapor is not adsorbed by microspheres, the third condition defines the law of water adsorbed on the binder surface.

Adsorbed mass of water vapor on the surface boundary $s_{24}$ inside $\omega'$ is accounted by the formula

$$\frac{\partial \rho_{42}}{\partial t} = -\beta_w (\langle \rho_{42} \rangle_{s_{24}} - a(\langle p_{22} \rangle_2, T)).$$

4. Geometrical structure and averaged parameters of a composite particle

Main geometrical parameters of the inner composite particles structure are defined using the averaging method. Chosen volume $\omega'$ in a neighborhood of a point $\xi$ is divided into subvolumes as follows

$$\omega' = \omega_2 \cup \omega_3 \cup \omega_4, \quad \omega_3 = \omega_{31} \cup \omega_{32},$$

where $\omega_2$, $\omega_3$, $\omega_4$ – non intersecting parts of $\omega$, defining free, occupied by microspheres and porous binder volumes; $\omega_{31}$, $\omega_{32}$ – non intersecting parts of $\omega_3$ defining the volume of a solid shell and cavity respectively.

Volume concentrations of phases and unit interphase surface area are defined by

$$l_2 = \omega_2 / \omega', \quad l_3 = \omega_3 / \omega', \quad l_{31} = \omega_{31} / \omega', \quad l_{32} = \omega_{32} / \omega', \quad l_4 = \omega_4 / \omega', \quad (13)$$

$$\alpha_{23} = s_{23} / \omega', \quad \alpha_{24} = s_{24} / \omega', \quad (14)$$

where $s_{23}$, $s_{24}$ – boundaries between free space and microspheres and binder inside $\omega'$. 

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Assuming all microspheres are the same and evenly distributed in space it is obvious that parameters $l_3, l_{31}, l_{32}, \alpha_{23}$ are constant and the following relations are valid

$$l_3 = l_{31} + l_{32}, \quad l_{31} = \beta^3 l_3, \quad l_{32} = (1 - \beta^3) l_3,$$

$$\alpha_{23} = \frac{3}{R} l_3,$$

where $R, r$ – microsphere and microsphere cavity radius; $\beta = r/R$ – microsphere structure coefficient.

Assuming that porous structure is distributed evenly in space suppose $l_4, \alpha_{24}$ and $l_2$ to be constants.

5. Mass transfer in granule in terms of averaged values

After averaging diffusion equation (9) in an infinite media consisting of evenly distributed microspheres and porous binder [2], one gets the following equations

$$\frac{\partial \langle \rho_2 \rangle_i}{\partial t} = D_i \Delta \langle \rho_2 \rangle_i + D_i \nabla \cdot \langle \alpha_{23} \langle \rho_2 n \rangle_{s23} + \alpha_{24} \langle \rho_2 n \rangle_{s24} \rangle +$$

$$+ \alpha_{23} D_i \langle \nabla_x \rho_2 \cdot n \rangle_{s23} + \alpha_{24} D_i \langle \nabla_x \rho_2 \cdot n \rangle_{s24}$$

$$+ \alpha_{23} \langle \rho_2 n \rangle_{s23} + \alpha_{24} \langle \rho_2 n \rangle_{s24} \approx - \langle \rho_2 \rangle_i^2 \nabla l_2.$$  

(17)

It is shown [2], that expressions under divergence operator in the second term in the right hand side of (17) being decomposed can be approximated in $\omega'$ as

$$\alpha_{23} \langle \rho_2 n \rangle_{s23} + \alpha_{24} \langle \rho_2 n \rangle_{s24} \approx - \langle \rho_2 \rangle_i^2 \nabla l_2.$$  

(18)

These terms describe the internal structure of phase distribution inside $\omega'$. Assuming $l_2$ to be constant they can be neglected. The third and the fourth terms in (17) are approximated using mass transfer conditions between phases (10) and (12).

6. Mathematical model

Consider gas mixture of helium and water vapor flows through a bed of composite adsorbent consisting of cylindrical particles in a certain space area $\Omega$ (adsorber). Mathematical model of such flow is described using averaged parameters. To simplify the notation suppose the following substitutions

$$\langle \rho_{1i} \rangle^1 \rightarrow \rho_{1i}, \quad \langle \rho_{2i} \rangle^2 \rightarrow \rho_{2i}, \quad \langle \rho_{3i} \rangle^3 \rightarrow \rho_{3i}, \quad \langle \rho_{42} \rangle_{s42} \rightarrow \rho_{42}, \quad \langle \mathbf{v}_1 \rangle_1 \rightarrow \mathbf{v}_1.$$

Parameters $\rho_{1i}, \mathbf{v}_1$ are functions of $(t, x)$, where $x \in \Omega$, and $t > 0$ – time. In every point of $\Omega$ inside a macro volume $\omega$ a mass transfer flux between free volume of adsorber and granules is calculated. Thus parameters $\rho_{2i}$ ($i = 1, 2$), $\rho_{31}, \rho_{42}$ are functions of $(t, x, \xi)$, where $x \in \Omega$, and $\xi \in G$, where $G$ – is a set of points, restricted by a cylinder surface $S_g$ of length $L_p$ and diameter $d_p$.

Gas mixture dynamics in adsorber $\Omega$ is described by the following relations

$$\frac{\partial \rho_{1i}}{\partial t} + \nabla \cdot \rho_{1i} \mathbf{v}_1 = K_{1i}, \quad K_{1i} = D_i \frac{m_1 m_2}{l_2} \int_{S_g} \nabla \xi \rho_{2i} ds \quad (i = 1, 2).$$

(19)
Helium dynamics inside composite adsorbent in $G$ is described by the following relations

$$\frac{\partial \rho_{21}}{\partial t} = D_1 \Delta \xi \rho_{21} + \frac{3 l_3 C_m \beta}{R d} \left( \frac{\rho_{31}}{l_{31}} - \frac{\rho_{21}}{l_2} \right),$$

$$\frac{\partial \rho_{31}}{\partial t} = -\frac{3 l_3 C_m \beta}{R d} \left( \frac{\rho_{31}}{l_{31}} - \frac{\rho_{21}}{l_2} \right),$$

with

$$\rho_{21}|_{S_g} = \rho_{11} l_2 / m_1.$$

Water vapor dynamics inside composite adsorbent in $G$ is described by the following relations

$$\frac{\partial \rho_{22}}{\partial t} = D_2 \Delta \xi \rho_{22} + \alpha_{24} \beta_w \left( \rho_{42} - a(\rho_{22}/l_2, T) \right),$$

$$\frac{\partial \rho_{42}}{\partial t} = -\beta_w \left( \rho_{42} - a(\rho_{22}/l_2, T) \right),$$

with

$$\rho_{22}|_{S_g} = \rho_{12} l_2 / m_1.$$

7. Conclusion

In the framework of the phenomena [1], which showed the possibility of creating a technology for the separating helium from natural gas, a mathematical model is obtained which describes the dynamics of a mixture of helium and water vapor through a porous medium, consisting of cylindrical granules of a composite adsorbent capable of retaining and subsequently releasing helium and water vapor.

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