Simulation of the multi-component gas transfer through porous adsorbent in the model of competing adsorption

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Abstract. In the framework of the competing adsorption model in the limit of strong adsorption a model of mass transfer of two-component gas through an absorbing porous body was developed. The model includes a system of two related equations. The first integral of the system is found, by which the problem is converted to a self-similar form. Two criteria relations defining the type of problem solution are established. The first of them includes the ratio of the threshold adsorption concentrations. At values of this parameter greater than 100 or less than 0.01, a pronounced displacement of one of the gas components inward the adsorbent is observed. The second parameter is proportional to the ratio of the initial concentrations of components and affects the mass of gas components absorbed by the adsorbent. Self-similar expressions are obtained for the distribution of the absorbed mass and the total absorbed mass of the gas components. For the air-titanium system, barothermal relationships of the depth of gas penetration into the adsorbent and the absorbed mass of components are calculated. It was found that for nitrogen-oxygen air mixture, the masses of absorbed nitrogen and oxygen by porous titanium practically coincide.

1. Introduction
The interaction of porous materials, in particular, titanium, with the components of the gas medium, is important in the sintering processes of powder materials, in the heat treatment of porous materials, in their diffusion welding, in the purification of inert gases from active impurities by porous adsorbents. In all the cases, the result of the interaction is a change in the physical and chemical characteristics of the porous titanium material and its properties. Such changes can be both the goal of the process and a negative factor hindering its implementation. In both cases, the actual task is to predict the development of these processes. The possibility to forecast the result allows one to design rational technological operations of processing porous titanium materials, to estimate the resource of effective use of fine filters. Due to the complexity of the experimental study of the interaction of porous titanium with active components of a multicomponent gas medium, the main method of analysis is the modeling of processes.

2. Actuality
The physical-chemical and microstructural state of the contact surfaces and volume of porous titanium materials are determined by the development of interaction with active gas impurities of the protective media. Currently, one can find data on the processes of oxidation and nitriding of titanium, both at atmospheric and at low pressures [1-9]. For simple titanium, these processes were studied for single-
component media [10-12], without taking into account the actual composition of the protective medium or residual gases during vacuuming. Features of the transfer of multi-component gases in the channels of the porous adsorbent require the development of existing models [13-17] of such processes. In the previous paper [18] the authors developed a simplified model under the assumption of complete displacement of nitrogen by oxygen on the surface of the adsorbent. A more realistic model should take into account the competing adsorption process which is typical for titanium [19]. In this paper such a model is formulated and studied at the limit of strong adsorption.

3. Problem statement

Nitrogen and oxygen are gas medium components which are actively interacting with titanium. Therefore, we will limit ourselves to consideration of the process which is typical for transfer and absorption of a nitrogen-oxygen mixture from ambient air into the porous titanium adsorbent. We will use the following simplifications that are reasonable for a process conducted at high temperatures.

1. In the depth of the titanium adsorbent, an area with ultra-low nitrogen and oxygen pressure is formed (self-evacuated zone [9,10]). We assume the gas pressure to be zero in this zone.
2. In the rest of the adsorbent (transfer zone), the transfer is carried out according to Darcy law [20,21].
3. In the transfer zone, the limit of strong adsorption is used, in which the sum of the degrees of filling the surface with gas components is equal to one.
4. As numerous experimental results show [2–7], the absorption rate of pure nitrogen and oxygen by titanium is independent of the gas pressure over a wide range of pressure values. Therefore, in the transfer zone, the absorption constants for these gases are proportional to their degrees of surface filling.
5. The pressures at which the mean free path of the gas molecules exceeds the pore diameter are considered, so the gas is transferred at the molecular condition [13]. In the same approximation, the transfer of the gas components is considered to be independent.
6. At high temperatures the rate of gas absorption by titanium is much higher than the rate of change in the gas concentration in the pore volume, so a quasi-stationary approximation is used to describe the transfer [13]. In this approximation, the rate of change in the volume concentration of gas components is neglected.

Next, we formulate and investigate a mathematical model of the transfer process within the framework of the assumptions made.

4. Theoretical part

Let us write the system of equations of the two-component gas transfer in the strong adsorbent using the model of competing adsorption.

The gas transfer and absorption occurs only in absorption zone, and distribution of the gas components is described by the related quasi-stationary equations of diffusion type [13, 16]

\[
\begin{align*}
D_1 \frac{\partial^2 n_1}{\partial x^2} &= \frac{\alpha \rho K_{11}}{\sqrt{t-t_0(x)}} \theta_1, \quad 0 < x < x_0(t) , \\
D_2 \frac{\partial^2 n_2}{\partial x^2} &= \frac{\alpha \rho K_{22}}{\sqrt{t-t_0(x)}} \theta_2,
\end{align*}
\]

where \(\theta_1\) and \(\theta_2\) are the degrees of surface filling with the gas components, which are expressed at the limit of strong adsorption in the form

\[
\theta_i = n_i / n_{i1}, \quad i = (1, 2)
\]
Here $D_1$ and $D_2$ are the effective diffusion coefficients of the gas components in a porous medium (the values of this coefficients are proportional to the filtration coefficient), $\alpha$ and $\rho$ are the specific surface area and density of the porous adsorbent respectively, $K_1$ and $K_2$ are the constants of absorption (for oxygen and nitrogen by titanium \([1-8]\)), $x_0(t)$ is the boundary coordinate of the gas transfer area, $t_0(x)$ is the inverse function to $x_0(t)$, and $n_u$ are the threshold concentrations for strong adsorption of the gas components. According to the formulae (2) the relationship

$$\theta_1 + \theta_2 = 1$$

(3)

takes place.

The boundary conditions to the system of equations (1) are the given gas components concentration $n_{i0}$ and $n_{20}$ in the external environment and the conditions of agreement at the boundary of the gas absorption area:

$$n_i(0,t) = n_{i0}, \quad n_i(x_0,t) = 0, \quad \frac{\partial n_i}{\partial x}(x_0,t) = 0, \quad i = (1, 2)$$

(4)

To research on the solution of the system (1), we divide the equations by $\alpha\rho K_i$ and add them taking into account the relationship (3):

$$\frac{\partial^2 N}{\partial x^2} = \frac{1}{\sqrt{t-t_0(x)}}, \quad 0 < x < x_0(t),$$

(5)

where we denote

$$N = \frac{D_1n_1}{\alpha\rho K_1} + \frac{D_2n_2}{\alpha\rho K_2}.$$  

(6)

According to expressions (4) and (6), the boundary conditions for the equation (5) are

$$N(0,t) = N_0 = \frac{D_1n_{10}}{\alpha\rho K_1} + \frac{D_2n_{20}}{\alpha\rho K_2}, \quad N(x_0,t) = 0, \quad \frac{\partial N}{\partial x}(x_0,t) = 0.$$  

(7)

The solution of the problem (5), (7) is obtained in \([13, 18]\) and has the form

$$N(x,t) = N_0\eta \left( \frac{x}{x_0(t)} \right), \quad x_0(t) = \frac{4}{\sqrt{\pi}}\sqrt{N_0 t}.$$  

(8)

The explicit form of the function $\eta(\xi)$ is given in \([13, 18]\). The solution (8) generalizes the result obtained in \([18]\) on the depth of gas penetration to porous body, in the framework of the model of competing adsorption.

Based on solution (8), we introduce a self-similar variable

$$\xi = x/x_0(t) = Ax/t^{1/4}, \quad A = 0.5(\pi/N_0)^{1/2}$$

(9)

and will replace the dependent variables

$$m_i(\xi) = \frac{D_1n_i/K_i}{D_1n_{10}/K_1 + D_2n_{20}/K_2}, \quad i = (1, 2).$$

(10)

As a result, the system (1) is transformed to a universal dimensionless form
\[
\begin{align*}
\frac{d^2 m_1}{d \xi^2} &= \frac{4}{\pi} \frac{m_1}{m_1 + \beta m_2} \left(1 - \xi^4\right)^{-1/2}, \\
0 < \xi < 1,
\end{align*}
\]
with the boundary conditions
\[
m_i(0) = m_{i0}, \quad m_i(1) = 0, \quad i = (1, 2),
\]
and the conditions \( m'_i(1) = 0 \) are satisfied identically. Here accordingly to the expressions (4) and (10)
\[
m_{10} = \frac{1}{1 + \gamma}, \quad m_{20} = \frac{\gamma}{1 + \gamma}.
\]
In the expressions (11) and (13) we introduce the criteria relations
\[
\beta = \frac{D_2 K_2 n_{12}}{D_2 K_2 n_{20}}, \quad \gamma = \frac{D_2 K_2 n_{12}}{D_2 K_2 n_{10}}.
\]
As a result, the solution of the problem (11)-(13) is defined only by two parameters (14) and satisfies additional relations
\[
m_1(\xi) + m_2(\xi) = \eta(\xi), \quad m_{10} + m_{20} = 1.
\]
Basically, the first of the relation (15) allows us to transform the system (11) into a single equation. However, it is not possible to obtain an analytical solution of such an equation, and for numerical solution of the problem, it is more convenient to formulate it in the form of (11). The difference scheme based on the system (11)-(13) is easily solved by simple iterations.

The results of numerical solution of the problem (11) and (12) for the different parameter values of the parameters are shown in figure 1. The accuracy of the calculation was checked by the beginning of the relations (15), which must be performed identically.

**Figure 1.** The dependence of the self-similar distribution of gas component concentrations (component 1 – solid lines, component 2 – dashed lines, function \( \eta \) – dotted lines) on the parameters \( \beta \) (left picture: 1 – \( \beta = 1 \); 2 – \( \beta = 0.1 \); 3 – \( \beta = 0.01 \)) and \( \gamma \) (right picture: 1 – \( \gamma = 0.2 \); 2 – \( \gamma = 1 \); 3 – \( \gamma = 5 \)).
We then obtain the distribution of the absorbed mass of the components along the direction of the gas flow (per unit area of the adsorbent). To do this, we integrate the source densities from the equations (1) over time using the variable (9).

As a result, we get

\[ q_i(x,t) = \alpha \rho K_i \int_{t_i(x)}^{t} \frac{\theta \delta r'}{\sqrt{t'-t_i(x)}}, \quad 0 < x < x_0(t). \]

We convert this expression using the variable (9):

\[ q_i(x,t) = 4 \alpha \rho K_i t^{1/2} \cdot \psi_i(\xi), \quad \psi_i(\xi) = \xi^2 \int_{\xi}^{1} \frac{\theta \delta \xi'}{\xi^{\epsilon^3} \sqrt{1-\epsilon^4}}, \quad \xi = x / x_0(t). \quad (16) \]

The solution (16) shows that the distribution form of the absorbed component does not change over time. Also the sum \( \psi_1(\xi) + \psi_2(\xi) \) does not depend on the parameters \( \beta \) and \( \gamma \).

The total mass of the component absorbed by the adsorbent area unit can be found, if we integrate the distribution (16) along the \( x \)-coordinate. However it is easier to integrate the component flow density into the adsorbent over time:

\[ Q_i(t) = - \int_{t_i(x)}^{t} D_i \frac{\delta n_i}{\delta x}(0,t') \, dt'. \]

Using the variable (9) and the solution (8) here, we get

\[ Q_i(t) = \alpha \rho K_i x_0(t)^{1/2} \cdot g_i(\beta,\gamma), \quad g_i(\beta,\gamma) = -\frac{\pi}{3} \frac{\delta n_i}{\delta \xi}(0). \quad (17) \]

Here the coefficients \( g_i \) depend only on the parameters \( \beta \) and \( \gamma \). However, due to the ratio (15), the sum \( g_1(\beta,\gamma) + g_2(\beta,\gamma) = -\pi \eta'(0)/3 \approx 1.748 \) does not depend on these parameters. The relationship between the absorbed mass of the component and time of the form \( t^{3/4} \) (17) was also obtained in [18] in the framework of a simplified model, but with the coefficients different from (17).

The study of solution (16) shows (figure 2) that an increase or decrease in parameter \( \beta \) from unit leads to the displacement of absorption of one of the gas components inward the adsorbent. In this case the real absorption depth of the other component becomes less than \( x_0 \). This behavior becomes expressed at \( \beta < 0.01 \) or \( \beta > 100 \) (strong competing adsorption) and was used in [18] as an assumption.

Figure 2. The relationship between the distribution of the absorbed mass of components (1 – solid line, 2 – dashed line) and the parameter \( \beta \).

Figure 3. The relationship between the coefficient \( g_1 \) and the criteria parameters \( \beta, \gamma \). The coefficient \( g_2 \) is found as \( g_2 = 1.748 - g_1 \).
Analysis of the coefficients gᵢ shows (figure 3) that their values change slightly with parameter β and significantly depend on parameter γ, that is, on the ratio of the partial concentrations of gas components in the environment.

The considered model can be easily generalized to any number of the gas components.

5. Discussion

We apply the obtained solutions to the description of air transport through a titanium adsorbent.

We consider the titanium adsorbent obtained by pressing the titanium powder particles of spherical shape with a diameter of d. In this case, the physical characteristics of the adsorbent – the effective diffusion coefficient and specific surface area – can be expressed in terms of a particle diameter and porosity of the material [20,21].

We use the experimentally measured values of the absorption constants of air components – oxygen and nitrogen [1-8]

\[
K_1 = 230e^{\frac{172500}{RT}} \left[ \frac{g}{cm^2 \cdot s^{1/2}} \right], \quad K_2 = 15e^{\frac{137100}{RT}} \left[ \frac{g}{cm^2 \cdot s^{1/2}} \right].
\]  

(18)

Here \( R \) is the universal gas constant, and \( T \) is the absolute temperature.

The calculations were carried out for the temperature range of 800–1000°C, the air pressure range of \( 10^2–10^5 \) Pa, the particle diameters of 10 µm, the duration of the time interval of 1 hour and the porosity of the adsorbent of 20%. Since oxygen and nitrogen are similar in the nature of interaction with titanium, we used the Arrhenius relationship for the ratio of the threshold adsorption concentrations \( n_{12}/n_{22} = \exp(-\Delta E/RT) \) and took a reasonable value of \( \Delta E = 45 \) kJ/mol as the binding energy difference.

According to the relations (14) and (18), the criteria relations β and γ in the analyzed system depend only on the temperature (figure 4).

The results of the calculation of the typical oxygen and nitrogen distribution are shown in figure 5. The shape of this distribution does not depend on the absolute air pressure and is determined only by the ratio of the partial pressures of oxygen and nitrogen (parameter γ).

The value of the depth penetration of air into porous titanium (figure 6) was slightly higher than in the simplified model [18]. In addition we can calculate the distribution of the absorbed mass of nitrogen and oxygen over the depth of the titanium adsorbent (figure 7). This distribution shows the displacement of the nitrogen absorption zone inward the porous titanium.
The results of the calculation of the absorbed mass of the oxygen and nitrogen relative to the temperature and pressure are shown in figure 8. In our calculation the amounts of nitrogen and oxygen absorbed are almost the same at all pressures and operating temperatures.

The presented numerical results are in agreement with the available experimental data on the penetration of residual gases into a porous titanium blank [9].

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