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Effect of adsorbent grain size on the pressure swing adsorption

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An analytical solution is obtained for a system of differential equations consisting of the equation for diffusion and absorption of a component in adsorbent grains and the balance equation for this component moving in the adsorbent layer. The technique for calculation of steady-state periodic adsorption processes based on expansion of a concentration signal into Fourier series of eigenfrequencies of this adsorption process is proposed. After decomposition each of the eigenwaves independently of the others is passed through the adsorbent layer, and at the output from this layer all this solutions for individual eigenwaves are summed. The solution to a problem of passing an arbitrary periodic concentration signal through the adsorbent layer is obtained as a result of summing the solutions for individual eigenwaves. The proposed method takes into account nonstationary diffusion processes inside the adsorbent grains. It makes possible to analyze effect of the adsorbent grain sizes on a pressure swing adsorption processes.

Keywords: Adsorption; Pressure swing adsorption; Adsorbent grain; Periodic process; Fourier series.

Вплив розміру зерна адсорбента на процеси безнагрівної короткоциклової адсорбції

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Отримано аналітичне рішення для системи диференціальних рівнянь, що складається з рівняння для дифузії та поглинання компонента в зернах адсорбенту та рівняння матеріального балансу для компонента, що рухається всередині адсорбційного шару. Запропоновано нову методику розрахунку сталих періодичних адсорбційних процесів на основі розкладання концентраційного сигналу в ряд Фур'є за власними частотами цього адсорбційного процесу. Після розкладання кожна власна концентраційна хвиля незалежно від інших пропускається через адсорбційний шар, а на виході з цього шару всі рішення для окремих власних хвиль знову об'єднуються. Рішення проблеми проходження довільного періодичного концентраційного сигналу крізь адсорбційний шар отримується в результаті підсумовування рішень для окремих власних концентраційних хвиль. Запропонований метод враховує нестаціонарні дифузійні процеси всередині зерен адсорбенту. Це дає змогу проаналізувати вплив розмірів зерен адсорбенту на процеси безнагрівної короткоциклової адсорбції.

Ключові слова: Адсорбція; Безнагрівна короткоциклова адсорбція; Зерно адсорбенту; Періодичний процес; Ряди Фур'є.

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1. Introduction

The statics of adsorption processes have been well studied over the past 50 years and brought to engineering calculation techniques suitable for practical use.

Moreover, the parameters which are necessary to calculate statics of adsorption are certificates data to adsorbents available on a market. These parameters are measured by standard methods and can be determined individually for each batch of adsorbent.

Therefore, the calculations of adsorption devices, whose operation is determined mainly by the static sorption, for example, adsorbers designed to remove trace impurities from technical gases, are carried out with accuracy sufficient for engineering applications.

A completely different situation occurs in the design of adsorption devices whose operation is determined mainly by the sorption kinetics and dynamics. Such devices are used in a pressure swing adsorption plants, which are used to separate gas mixtures. The existing methods for calculating such installations are too complex for practical application. In addition, these techniques have insufficient predictive power, as they usually need a number of empirical parameters that can only be obtained from a pilot plant of this type [1].

In this paper we propose a new method of calculating the pressure swing adsorption processes suitable for describing steady periodic processes of adsorption and, at the same time, relatively simple to implement.

2. Material and methods

2.1. Effect of adsorbent grain size

For a more complete account of the effect of adsorbent grain size on the pressure swing adsorption processes was used wave model of periodic adsorption

described in the [2].

This model makes it possible to calculate non-stationary adsorption processes with a variable gas composition at the inlet to the adsorption apparatus.

In the mathematical description of adsorption of a gas mixture component, as in [2], the following pattern was adopted for propagation of this component in a porous layer of adsorbent.

The component of interest to us will be considered dissolved in a non-adsorbed carrier gas, which is filtered at a constant rate through the adsorbent bed. The use of a carrier gas in the model is equivalent to accepting hypothesis that there is no longitudinal mixing of the gas component in the adsorber.

In addition, the carrier gas, which moves at a constant speed, serves as a moving frame of reference, relative to which the phase shift of the concentration waves of absorbed component is determined.

Therefore, the carrier gas is an abstract element of the mathematical model and its presence is not necessary for the physical realization of this model.

Near the contact points of the adsorbent grains, stagnant zones are formed in which the gas is practically stationary.

The flow of the carrier gas with the dissolved component passes through a chain of cavities and voids in the space between the adsorbent grains.

Thus, the entire space in which the adsorbent is located is conventionally divided into two parts: a fixed framework of adsorbent grains together with adjoining stagnant zones, and a system of interconnected voids and channels in which the carrier gas moves with the adsorbed component dissolved in it.

In the fixed framework, distribution of the component of interest to us mainly occurs due to molecular diffusion in the carrier gas filling the adsorbent pores and stagnant zones around them.

In the system of channels located between the grains of the adsorbent the component is transferred mainly through convection.

In the proposed formulation of the problem, the withdrawal of the component from the fixed framework to the moving carrier gas is considered as outflow of this component in a problem of molecular diffusion in the fixed framework. Convection of the component in channels with a moving carrier gas is described by a separate equation of material balance of this component.

Taking this into account, the first differential equation of molecular diffusion in a fixed framework can be written as:

$$D_E \frac{\partial^2 C(x,y,\tau)}{\partial x^2} + D_E \frac{\partial^2 C(x,y,\tau)}{\partial y^2} -$$
$$\beta \cdot F\left[C(x,y,\tau) - Cg(x,\tau)\right] = K_G \frac{\partial C(x,y,\tau)}{\partial \tau}, \quad (1)$$

where $C(x,y,\tau)$ is the current volume concentration of the component in the fixed framework (in the gas located in the adsorbent pores and stagnant zones, around the adsorbent grains), $[m^3/m^3]$;

$Cg(x,\tau)$ is the current volume concentration of the component in a moving carrier gas, $[m^3/m^3]$;

β is the mass transfer coefficient between gas in the fixed framework and gas moving in cavities between grains of the adsorbent, $[m^3/(s \cdot m^2)]$;

F is the specific surface area of the fixed framework, $[m^2/m^3]$.

D_E is the equivalent value of the sorbate diffusion coefficient in the adsorbent grain, taking into account the diffusion features in the porous body: the relative pore volume, the variable pore cross section, the presence of dead-end pores, etc., $[m^2/s]$.

$K_G = \left(\frac{da}{dC}\right)_{T=const}$ is the dimensionless form of the

Henry constant for adsorption of the component, where a is an adsorption of this component, expressed in cubic meters of sorbate per 1 m^3 of bulk volume of the adsorbent.

In reported differential equation for diffusion of a component in a fixed framework, the Henry constant is present. This means that in the proposed mathematical model, a linear model of adsorption of gas by adsorbent is adopted. The adsorption isotherm corresponding to this model is known as a Henry isotherm. When selecting any other dependence to describe the adsorption of the component, we obtain a nonlinear equation for the diffusion of the component in the fixed framework, which either is not analytically solved, or its solution is too complicated.

The material balance of the component in the elementary volume of the carrier gas moving in the system of pores and the cavities between the grains of adsorbent can be written in the form of a one-dimensional differential equation:

$$\beta \cdot F\left[C(x,\delta,\tau) - Cg(x,\tau)\right] - G \cdot \frac{dCg(x,\tau)}{dx} = 0; \quad (2)$$

where G is the volumetric flow rate of the mixture of carrier gas and component assigned to the unit section of the adsorbent bed, $[m^3/s]$;

δ is the characteristic grain size in the adsorbent bed, $[m]$.

These two equations combined allow us to find a distribution of concentration of the component in the moving carrier gas and in the fixed framework.

Thus, the problem of diffusion and adsorption of the component in a flat layer of the adsorbent, which is flow around by a carrier gas, is actually solved. The calculation scheme of this task is shown in Fig. 2.

Since this mathematical model takes into account a specific surface of the fixed framework F, then together with the characteristic grain size δ, this makes it possible to accurately take into account a shape and dimensions of the grains of the used adsorbent.

The solution of the system of equations obtained is analogous to the solution described in [2].

After transition to the operator form with respect to time, equation (1) takes the form:

$$\frac{\partial^2 C(x,y,s)}{\partial x^2} + \frac{\partial^2 C(x,y,s)}{\partial y^2} =$$
$$= \frac{K_G}{D_E} \cdot \left[s \cdot C(x,y,s) - Co(x,y)\right] + \quad (3)$$
$$+ \frac{\beta \cdot F}{D_E}\left(C(x,y,s) - Cg(x,s)\right);$$

where s is the time differentiation operator [3];

$Co(x, y)$ is the initial distribution of the component concentration in the adsorption layer.

We shall further assume for simplicity that the initial distribution of the component concentration is zero.

We carry out finite Fourier integral transformation with respect to coordinate x, choosing the cosine function as a kernel of the transformation [4]:

$$\overline{\overline{C}}_k(y,s) = \int_0^h C(x,y,s)\cos\left(2\pi \cdot k\frac{x}{h}\right)dx; \quad k = 0,1,2... \quad (4)$$

When this form of the finite Fourier integral transformation kernel is chosen, zero boundary conditions of a second kind are automatically provided on the ends of the fixed framework.

After carrying out the finite Fourier integral transformation with respect to the coordinate x, equation (1) takes the form:

$$-\frac{(2\pi \cdot k)^2}{h^2}\overline{\overline{C}}_k(y,s) + \frac{\partial^2 \overline{\overline{C}}_k(y,s)}{\partial y^2} =$$

$$= \left(\frac{K_G}{D_E} \cdot s\right)\cdot \overline{\overline{C}}_k(y,s) + \frac{\beta \cdot F}{D_E}\left[\overline{\overline{C}}_k(y,s) - \overline{\overline{Cg}}_k(s)\right]. \quad (5)$$

We carry out the finite Fourier integral transformation with respect to the y coordinate, using the transformation kernel, which has the form:

$$\overline{\overline{C}}_{k,n}(s) = \int_0^\delta \overline{\overline{C}}_k(y,s)\cos\left(\mu_n\frac{y}{\delta}\right)dy;$$

$$n = 0,1,2... \quad (6)$$

We find the eigenvalues of the finite Fourier integral transformation μ_n so as to ensure that the boundary condition of third-type is satisfied on the free surface of grains and zero boundary condition of the second kind on the grain symmetry axis.

To find the values of the finite Fourier integral transformation, we use the transcendental equation:

$$\left(\frac{\mu_n}{\delta}\right)\cdot \tan(\mu_n) = \frac{\beta \cdot F}{D_E}. \quad (7)$$

After cosine Fourier integral transformation along the coordinate y, the diffusion equation in the fixed framework becomes:

$$-\frac{(2\pi \cdot k)^2}{h^2}\overline{\overline{C}}_{k,n}(s) - \frac{\mu_n^2}{\delta^2}\overline{\overline{C}}_{k,n}(s) =$$

$$= \left(\frac{K_G}{D_E} \cdot s\right)\cdot \overline{\overline{C}}_{k,n}(s) + \quad (8)$$

$$+ \frac{\beta \cdot F}{D_E}\left[\overline{\overline{C}}_{k,n}(s) - \overline{\overline{Cg}}_k(s)\frac{\mu_n}{\delta}\sin(\mu_n)\right].$$

From this we find the image of a function describing the component concentration in the fixed framework:

$$\overline{\overline{C}}_{k,n}(s) = \frac{\overline{\overline{Cg}}_k(s)\frac{\beta \cdot F}{D_E}\frac{\mu_n}{\delta}\sin(\mu_n)}{\left(\left(\frac{(2\pi \cdot k)^2}{h^2} + \frac{\mu_n^2}{\delta^2} + \frac{\beta \cdot F}{D_E}\right) + \frac{K_G}{D_E} \cdot s\right)}.$$

$$(9)$$

This equation allows us to find solution of the diffusion equation in the fixed framework in the form of a double Fourier series:

$$C(x,y,s) = \frac{2}{h}\frac{\beta \cdot F}{D_E} \times$$

$$\times \sum_n \left\{ \begin{array}{l} \frac{\mu_n}{\delta}\sin(\mu_n)\frac{2}{\delta}\cos\left(\mu_n\frac{y}{\delta}\right)\times \\ \times \sum_k \frac{\overline{\overline{Cg}}_k(s)\cdot\cos\left(2\pi \cdot k\frac{x}{h}\right)}{\left(\frac{(2\pi \cdot k)^2}{h^2} + \frac{\mu_n^2}{\delta^2} + \frac{K_G}{D_E} \cdot s + \frac{\beta \cdot F}{D_E}\right)} \end{array} \right\}. \quad (10)$$

Where the coefficients $\overline{\overline{Cg}}_k(s)$ are independent of coordinates and are found by the formula:

$$\overline{\overline{Cg}}_k(s) = \int_0^h Cg(x,s)\cdot\cos\left(2\pi \cdot k\frac{x}{h}\right)dx. \quad (11)$$

Up to now, the solution of the diffusion equation of a component in a fixed framework has been carried out by the method of finite integral transformations described in the scientific and technical literature [4].

Let us determine the wave character of the oscillations of component concentration in the carrier gas. Moreover, we choose not arbitrary frequencies of concentration oscillations, but the eigenfrequencies of the given adsorption process.

The eigenfrequencies is the frequencies at which an integer number of concentration waves are laid along the thickness of the adsorption layer:
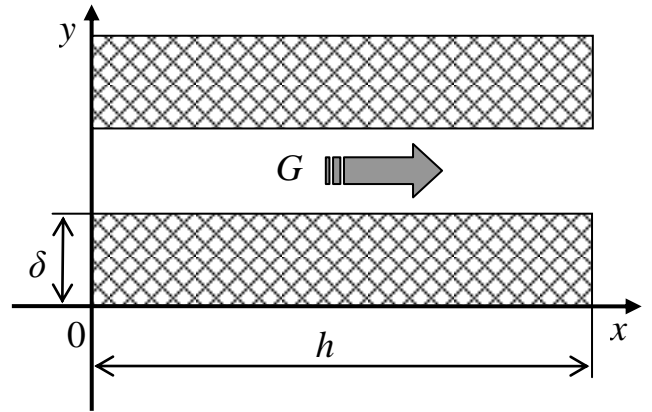

Figure 2 - Calculation scheme for wave adsorption of component.

$$Cg(x,\tau) = A_k\cos\left(2\pi \cdot k\left(\frac{x}{h} + \frac{\tau}{T}\right)\right) =$$

$$= A_k\left[\begin{array}{l} \cos\left(2\pi \cdot k\frac{x}{h}\right)\cos\left(2\pi \cdot k\frac{\tau}{T}\right) - \\ -\sin\left(2\pi \cdot k\frac{x}{h}\right)\sin\left(2\pi \cdot k\frac{\tau}{T}\right) \end{array}\right]. \quad (12)$$

where T is the period of eigen oscillations of the concentration of the component, [s];

A_k is the amplitude of the oscillations of the component concentration in the carrier gas moving inside the adsorbent bed [m³/m³].

We construct a finite integral cosine transformation with respect to the coordinate x:

$$\overline{\overline{Cg}}_m(\tau) = \int_0^h Cg(x,\tau)\cos\left(2\pi \cdot m\frac{x}{h}\right)dx =$$
$$= A_k \cos\left(2\pi \cdot k\frac{\tau}{T}\right)\int_0^h \cos\left(2\pi \cdot k\frac{x}{h}\right)\cos\left(2\pi \cdot m\frac{x}{h}\right)dx -$$
$$- A_k \sin\left(\pi \cdot k\frac{\tau}{T}\right)\int_0^h \cos\left(2\pi \cdot k\frac{x}{h}\right)\sin\left(2\pi \cdot m\frac{x}{h}\right)dx$$

(13)

To find the integrals obtained, we use the mutual orthogonality of the concentration eigenwaves, which is determined by the equation:

$$\int_0^h \cos\left(2\pi k\frac{x}{h}\right)\cos\left(2\pi m\frac{x}{h}\right)dx = \frac{h}{2},\_\text{if}\{m=k\}$$

$$\int_0^h \cos\left(2\pi k\frac{x}{h}\right)\sin\left(2\pi m\frac{x}{h}\right)dx = 0,\_\text{if}\{m \neq k\}$$

(14)

With this in mind:

$$Cg_k(\tau) = A_k \cos\left(2\pi k\frac{\tau}{T}\right)\frac{h}{2}.\quad (15)$$

We pass to the operator form with the time differentiation operator:

$$\overline{\overline{Cg}}_k(s) = \frac{A_k h}{2}\frac{s}{\left(s^2 + \left(\frac{\pi k}{T}\right)^2\right)}.\quad (16)$$

The meaning of the last transformation is that if a concentration signal in the form of a harmonic wave whose frequency coincides with one of the eigenfrequencies of the adsorption layer to which this concentration signal is fed, then all the coefficients of the Fourier series, except one, will be equal to zero. The solution of the diffusion equation in this case can be represented as a relatively simple finite expression in place of an infinite Fourier series in the general case.

As is known from the theory of oscillations, under forced oscillations of the system the frequency of these oscillations always coincides with the frequency of the external action that caused these oscillations. Therefore, the frequency of the concentration oscillations inside the grain of the adsorbent will coincide with the frequency of the concentration oscillations supplied from the outside into the adsorbent bed. In our case, this will be one of the eigenfrequencies for the adsorption layer under consideration. In this case, the length of the concentration waves propagating in the grain of the adsorbent, in general, differs from the length of the concentration wave in the layer of the adsorbent under consideration.

Let us consider a concrete example of the absorption of nitrogen from air in a layer of zeolite. The solution of such problems is necessary to the calculation of pressure swing adsorption installations designed to produce oxygen.

In this case, the equivalent diffusion coefficient of nitrogen in the zeolite grains is of the order of $D_E \approx 10^{-5}$ [m²/s], and the product of the mass transfer coefficient and the grain surface of the adsorbent $\beta F \approx 10$ [m³/s]. Therefore, the parameter $\beta F/D_E$ when the nitrogen is absorbed by the zeolite has values on the order of 10^6 [m]. The corresponding values μ_n found by formula (7) turn out to be very close to $(\pi + n\pi/2)$, where n is an integer.

This means that an integer number of concentration waves almost lay within the grain of the adsorbent. Therefore, we can use the selection rule (14) to simplify the solution for the coordinate y. But it should be remembered that in this case the selection rule is only approximate. Therefore, even a relatively small deviation from this equality can lead to a substantial deviation of the sum of the infinite Fourier series from the approximate value found in this way.

In the case under consideration, the sum of the Fourier series with respect to the y coordinate is approximately equal to the n-th term of this series, which corresponds to the n-th eigenwave of the adsorption layer. The approximate value of the Fourier series sum with respect to the coordinate y can be found by using the norm of the n-th harmonic, the square of which is equal to:

$$\|\psi_y\|_n^2 = \int_0^\delta \cos^2\left(\mu_n\frac{y}{\delta}\right)dy \quad (17).$$

The results of the calculations show that for zeolite grains whose diameter does not exceed 3-4 mm, such simplification does not lead to a significant error. This means that in most cases of practical importance, this equality is valid with sufficient accuracy for engineering calculations.

As a result, using the rule of frequency selection (14), we left only one term from the double Fourier series, for which $n=k$. Therefore, if the k-th concentration eigenwave arrives at the entrance of the adsorption layer, then for the steady regime, we obtain a relatively simple expression for the image of the concentration wave in the stationary framework:

$$\overline{\overline{C}}_{k,n}(s) = \frac{\dfrac{A_k h}{2}\dfrac{\beta F}{D_E}}{\left(\left(\dfrac{(2\pi \cdot k)^2}{h^2} + \dfrac{\mu_n^2}{\delta^2} + \dfrac{\beta F}{D_E}\right) + \dfrac{K_G}{D_E}\cdot s\right)} \times$$
$$\times \frac{\dfrac{\mu_n}{\delta}\sin(\mu_n)\cdot\|\psi_y\|_n^2 \cdot s}{\left(s^2 + \left(\dfrac{2\pi \cdot k}{T}\right)^2\right)}.$$

(18)

We decompose this expression into simple fractions, and expression involving two terms is result. The first term takes the form:

$$-\frac{\dfrac{A_k h}{2}\dfrac{\beta F}{D_E}}{\left(\left(\dfrac{(2\pi\cdot k)^2}{h^2}+\dfrac{\mu_n^{\,2}}{\delta^2}+\dfrac{\beta F}{D_E}\right)\cdot\dfrac{D_E}{K_G}+s\right)}\times$$

$$\times\frac{\dfrac{\mu_n}{\delta}\sin(\mu_n)\cdot\left\|\psi_y\right\|_n^2\cdot\left(\dfrac{(2\pi\cdot k)^2}{h^2}+\dfrac{\mu_n^{\,2}}{\delta^2}+\dfrac{\beta F}{D_{\text{э}}}\right)}{\left(\left(\dfrac{(2\pi\cdot k)^2}{h^2}+\dfrac{\mu_n^{\,2}}{\delta^2}+\dfrac{\beta F}{D_E}\right)^2+\left(\dfrac{K_G}{D_E}\right)^2\cdot\left(\dfrac{2\pi\cdot k}{T}\right)^2\right)}.$$

(19)

The original of this expression is an inverse exponential function of time. In the steady state this term tends to zero. Therefore, below we omit this term, since the problem of steady-state adsorption is considered.

The second term can be written in the form:

$$\overline{\overline{C}}_{k,n}(s)=$$

$$=\frac{\dfrac{A_k h}{2}\dfrac{\beta F}{D_E}\dfrac{\mu_n}{\delta}\sin(\mu_n)\cdot\left\|\psi_y\right\|_n^2}{\left(\left(\dfrac{(2\pi\cdot k)^2}{h^2}+\dfrac{\mu_n^{\,2}}{\delta^2}+\dfrac{\beta F}{D_E}\right)^2+\left(\dfrac{K_G}{D_E}\right)^2\cdot\left(\dfrac{2\pi\cdot k}{T}\right)^2\right)}\times$$

$$\times\left\{\frac{\left(\dfrac{K_G}{D_E}\right)\cdot\left(\dfrac{2\pi\cdot k}{T_k}\right)^2}{\left(s^2+\left(\dfrac{2\pi\cdot k}{T}\right)^2\right)}+\frac{\left(\dfrac{(2\pi\cdot k)^2}{h^2}+\dfrac{\mu_n^{\,2}}{\delta^2}+\dfrac{\beta F}{D_E}\right)s}{\left(s^2+\left(\dfrac{2\pi\cdot k}{T}\right)^2\right)}\right\}.$$

(20)

We pass to the original of this expression in time. To simplify its record, we introduce the following multi-index notation:

$$Ba_{k,n}=\frac{\dfrac{A_k h}{2}\dfrac{\beta F}{D_E}\dfrac{\mu_n}{\delta}\sin(\mu_n)}{\left[\left(\dfrac{(2\pi\cdot k)^2}{h^2}+\dfrac{\mu_n^{\,2}}{\delta^2}+\dfrac{\beta F}{D_E}\right)^2+\left(\dfrac{K_G}{D_E}\right)^2\left(\dfrac{2\pi\cdot k}{T}\right)^2\right]}$$

(21)

$$Bc_{k,n}=\left(\frac{(2\pi\cdot k)^2}{h^2}+\frac{\mu_n^{\,2}}{\delta^2}+\frac{\beta\cdot F}{D_E}\right)$$

(22)

$$Bs_k=\left(\frac{K_G}{D_E}\right)\cdot\left(\frac{2\pi\cdot k}{T}\right)$$

(23)

Then

$$\overline{\overline{C}}_{k,n}(\tau)=Ba_{k,n}\sqrt{\left(Bc_{k,n}\right)^2+\left(Bs_{k,n}\right)^2}\cdot\left\|\psi_y\right\|_n^2\times$$

$$\times\cos\left(\left(\frac{2\pi\cdot k}{T}\right)\tau-\varphi_{k,n}\right)\cos\left(\mu_n\frac{y}{\delta}\right)$$

(24)

Where

$$\varphi_{k,n}=\arccos\left(\frac{Bc_{k,n}}{\sqrt{\left(Bc_{k,n}\right)^2+\left(Bs_k\right)^2}}\right)=$$

$$=\arcsin\left(\frac{Bs_k}{\sqrt{\left(Bc_{k,n}\right)^2+\left(Bs_k\right)^2}}\right)=\arctan\left(\frac{Bs_{k,n}}{Bc_{k,n}}\right).$$

(25)

The physical meaning of this formula is quite obvious: the amplitude of the concentration oscillations in the stationary framework is proportional to the amplitude of the concentration oscillations in the carrier gas (at the entrance to the adsorbent bed) multiplied by a certain coefficient depending on the gas velocity and adsorbent properties.

The phase of the concentration oscillations in the stationary framework lags behind the phase of the concentration oscillations in the carrier gas at the inlet to the adsorbent bed.

Unlike sound or electromagnetic waves, waves of concentration are not reflected from the edges of the adsorption layer. Therefore, in the course of further transformations, the terms of the equations that describe the reflected concentration wave were discarded.

Taking this into account, the expression describing the change in the concentration of the component in the fixed framework pass into:

$$C_k(x,y,\tau)=\frac{2}{h}Ba_{k,n}\sqrt{\left(Bc_{k,n}\right)^2+\left(Bs_k\right)^2}\cdot\left\|\psi_y\right\|_n^2\times$$

$$\times\cos\left(2\pi\cdot k\left(\frac{\tau}{T}+\frac{x}{h}\right)-\varphi_k-\mu_k\frac{y}{\delta}\right)$$

(26)

If an integer number of waves are placed inside the grain of the adsorbent, then the value of the normalizing factor is equal to: $\left\|\psi_y\right\|_n^2=\dfrac{\delta}{2}$.

With this in mind, we have:

$$C_k(x,y,\tau)=\frac{2}{h}Ba_{k,n}\sqrt{\left(Bc_{k,n}\right)^2+\left(Bs_k\right)^2}\times$$

$$\times\frac{\delta}{2}\cos\left(2\pi\cdot k\left(\frac{\tau}{T}+\frac{x}{h}\right)-\varphi_k-\mu_k\frac{y}{\delta}\right).$$

(27)

The finite grain size of the adsorbent in this mathematical model is reflected in the additional phase shift of the concentration wave into the adsorbent grains and in adsorption layer.

The material balance of the component under consideration in elementary volume of the carrier gas moving within the fixed framework can be written in the form of differential equation (2). The physical meaning of this equation is that the change in concentration of the gas moving along a chain of voids between grains of adsorbent occurs only due to mass exchange with gas that is inside grains of adsorbent.

We construct the cosine Fourier transform with respect to coordinate x, taking into account the fact that in the accepted mathematical model only such oscillations of

the component concentration are considered for which the phases at the input and at the output are equal:

$$\overline{\overline{Cg}}_k(\tau) = \int_0^h Cg(x,\tau)\cos\left(2\pi \cdot k\frac{x}{h}\right)dx =$$
$$= Cg(h,\tau) - Cg(o,\tau) +$$
$$+ \frac{2\pi \cdot k}{h}\int_0^h Cg(x,\tau)\sin\left(2\pi \cdot k\frac{x}{h}\right)dx$$
$$= Cg(h,\tau) - Cg(o,\tau) + \frac{2\pi \cdot k}{h}\overline{\overline{Cg}}_k^s(\tau)$$
$$k = 0,1,2... \qquad (28)$$

With this in mind, equation (28) after the cosine transformation can be rewritten as:

$$Cg(h,\tau) - Cg(o,\tau) + \frac{2\pi \cdot k}{h}\overline{\overline{Cg}}_k^s(\tau) =$$
$$= \frac{\beta \cdot F}{G}\overline{\overline{C}}_k(\delta,\tau) - \frac{\beta \cdot F}{G}\overline{\overline{Cg}}_k^s(\tau). \qquad (29)$$

Just as in the author's paper [2], we will assume that in the steady-state regime concentration wave passing through the adsorbent layer, the mass of the adsorbed component remains unchanged. This is possible only if the length of the concentration wave in the adsorbent layer is equal to the thickness of this layer. Therefore, the difference in the instantaneous concentrations of the component in the carrier gas for the eigenwaves at the inlet and at the exit from this adsorbed layer is zero:

$$Cg(h,\tau) - Cg(o,\tau) = 0.$$

From this:

$$\frac{2\pi \cdot k}{h}\overline{\overline{Cg}}_k^s(\tau) = \frac{\beta \cdot F}{G}\left[\overline{\overline{C}}_k(\delta,\tau) - \overline{\overline{Cg}}_k^s(\tau)\right]. \quad (30)$$

It follows from this equation that if a cosine-wave of concentration propagates in fixed framework, then in carrier gas it generates a sine-wave of concentration with certain amplitude. This can be regarded as the spatial lag of the concentration wave in the carrier gas from the concentration wave in the fixed framework.

In steady state motion of a concentration wave, between carrier gas and adsorbent takes place multiple exchanges of component. As a result, the amplitudes of component mass oscillation in the carrier gas and in the adsorbent are identical.

The tangent of the angle of the spatial phase shift between the concentration oscillations in the fixed frame and in the carrier gas is defined as the ratio of amplitudes the sine and cosine components of these waves:

$$\omega_k = \arctan\left\{\frac{\overline{\overline{Cg}}_k^s(\tau)}{\overline{\overline{C}}_k(\delta,\tau) - \overline{\overline{Cg}}_k^s(\tau)}\right\} =$$
$$= \arctan\left\{\frac{\beta \cdot F \cdot h}{2\pi \cdot k \cdot G}\right\}. \qquad (31)$$

Unlike sound or electromagnetic waves, the amplitudes of concentration waves can not add together when interference. Because increasing in the concentration of a component without expenditure of energy contradicts the second law of thermodynamics.

When mixing two streams, the resulting concentration of the component is found as a weighted average of its concentrations in the streams that are mixed. Similarly, when the concentration waves are overlaid, the amplitude of the resultant wave is found as the average value of amplitudes of the concentration waves that interfere. In order to ensure the implementation of this condition in the case of interference of concentration waves, it is sufficient to take the amplitude of the concentration wave at the exit from the adsorption layer equal to half the amplitude of the concentration wave at the entrance to this adsorbent layer.

It follows that the amplitude of eigenoscillations of the component concentration at the outlet from adsorbent bed will be equal to half of oscillation amplitude at the entrance to this adsorbent bed:

$$\overline{A} = \frac{A_1 + A_2}{2} = \frac{A_1}{2} + \frac{A_2}{2}. \qquad (32)$$

In view of this, we obtain a comparatively simple solution to the concentration eigenwaves, at the outlet of adsorptive layer:

$$Cg_k(x,\tau) = \frac{A_k}{2}\cos\left[2\pi k\left(\frac{x}{h} + \frac{\tau}{T}\right) - \varphi_k - \mu_k - \omega_k\right]. (33)$$

The physical sense of this formula is obvious: for eigenwaves propagating through the adsorbent bed, its frequency remains the same, and the phase of the wave delayed in time by an angle $\varphi_k + \mu_n$, and lags in space on the angle ω_k. Moreover, phase angles are different for different concentration wave.

Equations (30) and (32) are derived in a different way in the author's work [2]. The derivation of these equations in various ways confirms their correctness.

Since any periodic concentration signal can be represented as a sum of harmonic oscillations, then, using a relatively simple solution obtained for the eigenwaves of the adsorption layer, we can easily obtain a solution for an arbitrary process of periodic operation of the adsorption apparatus in an unsteady but steady-state regime.

2.2. Application of the wave adsorption method for calculating a processes of pressure swing adsorption

Here, we demonstrate the potential of obtained solutions for calculating a pressure swing adsorption processes.

Consider the periodical process of nitrogen adsorption in a layer consisting of zeolite grains with a predetermined size. Such process is decisive for installations designed to produce oxygen using the pressure swing adsorption method.

As an example, let us consider the case where air is periodically supplied to the inlet of the adsorption apparatus in the form of a trapezoidal pulse with excess pressure of 0.8 bars. The adsorbent is regenerated in a vacuum. Operating time of the apparatus in the nitrogen uptake mode and regeneration time of the adsorbent are assumed to be same. The volumetric flow rate of air supplied to the adsorber and pumping speed (volume flow rate) of the vacuum pump are assumed to be equal. The low pressure
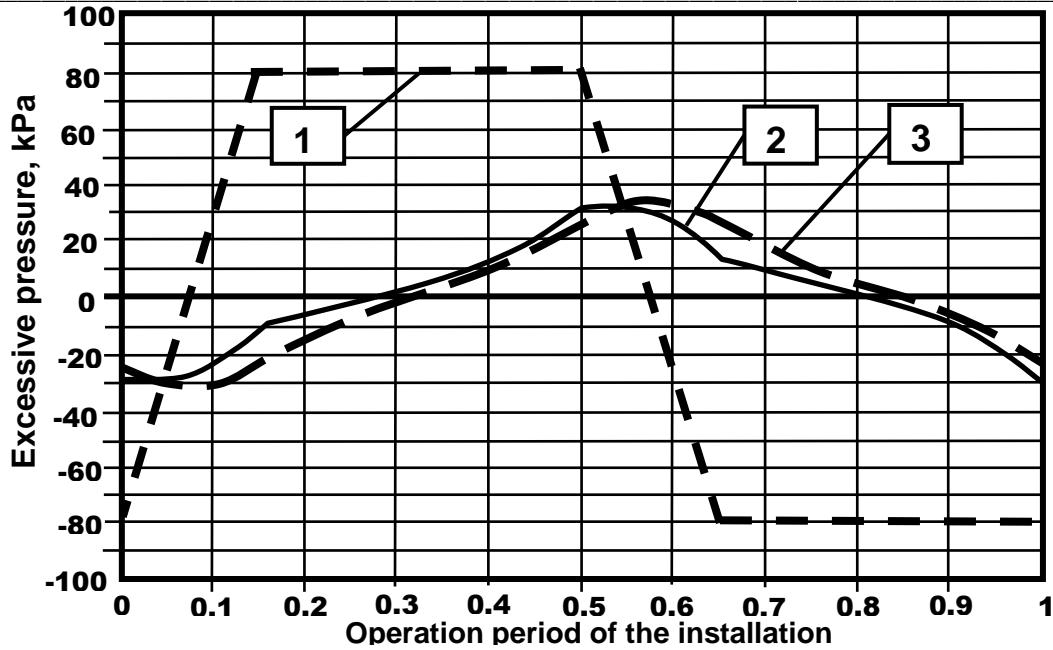
Figure 2. *Calculated dependences of the partial pressure of nitrogen in the carrier gas at the inlet to the adsorber, at the surface of the adsorbent grains and in the carrier gas at the exit from the adsorber.*

1 *is the partial pressure of nitrogen at the inlet to the adsorber;*

2 *is the partial pressure of nitrogen in the carrier gas exiting from the adsorber;*

3 *is the partial pressure of nitrogen on the surface of grains of the adsorbent.*

limit on this vacuum pump should be less than 0.2 bars.

Calculations are made for adsorption layer of height 1 m, period of operation of the adsorption apparatus in the absorption regime is assumed equal to 100 s. The grain size of the adsorbent is assumed equal to 2 mm, the air velocity in the adsorbent bed is assumed to be constant and equal to 0.1 m/s.

The dimensionless constant Henry for the absorption of nitrogen by the zeolite is taken equal to K_G=11.7, and the equivalent diffusion coefficient will be assumed equal to $2.4 \cdot 10^{-6}$ m^2/s.

The mass transfer coefficient from the adsorbent grains to carrier gas was determined from the formulas given in the literature [5].

The flexibility of the proposed method can be illustrated by the example when a linear change in pressure during the intake and discharge of gas from the adsorber are assumed. The duration of the processes of intake and exhaust is assumed equal to 15% of the operational period of the adsorption apparatus.

We decompose the trapezoidal pulse of the partial pressure of nitrogen into Fourier series. To determine coefficients of the expansion, we use known formulas from mathematical analysis:

$$a_k = \int_0^T f(\tau)\sin\left(2\pi k\frac{\tau}{T}\right)d\tau;$$

$$b_k = \int_0^T f(\tau)\cos\left(2\pi k\frac{\tau}{T}\right)d\tau; \qquad (37)$$

where $f(\tau)$ is a function expanded in Fourier series.

After this, using formulas (27) and (33), we find terms of Fourier series for the concentration of the component

absorbed in the fixed framework and for the concentration of the component in the carrier gas exiting the adsorber.

In this example, calculations were carried out for the first hundred terms of a Fourier series. This makes it possible to exclude oscillations that usually occur on calculated graphs when a Fourier series is finite.

Figure 2 shows the calculated curves for the nitrogen partial pressure at the inlet to the adsorber 1, the nitrogen partial pressure in the gas leaving the adsorber 2 and the partial pressure of nitrogen on the surface of the adsorbent grains 3 in the outlet section of the apparatus.

The form of obtained graphs corresponds to ideas about the physics of a processes taking place in the adsorber. At the stage of nitrogen adsorption, its partial pressure at the outlet from adsorber increases due to saturation of the adsorbent. At this stage, nitrogen partial pressure is somewhat greater than the partial pressure of nitrogen on the surface of the adsorbent grains. During the regeneration of the adsorbent the picture is reversed, the partial pressure of nitrogen at the outlet from the adsorber drops, and throughout the regeneration period, the pressure of nitrogen in the carrier gas remains lower than the pressure on the surface of the adsorbent.

An interesting feature of this graph is there are two points on that all three curves are intersect. This feature reflects the physics of the processes occurring in the apparatus.

When desorption of nitrogen is ends and the process of adsorption begins, the direction of nitrogen moving is changes. The partial pressure of nitrogen entering the adsorber becomes higher than its pressure on the surface of the adsorbent grains. As a result, the nitrogen partial pressure in the outlet gas from the adsorber also becomes higher than the pressure on the surface of the adsorbent
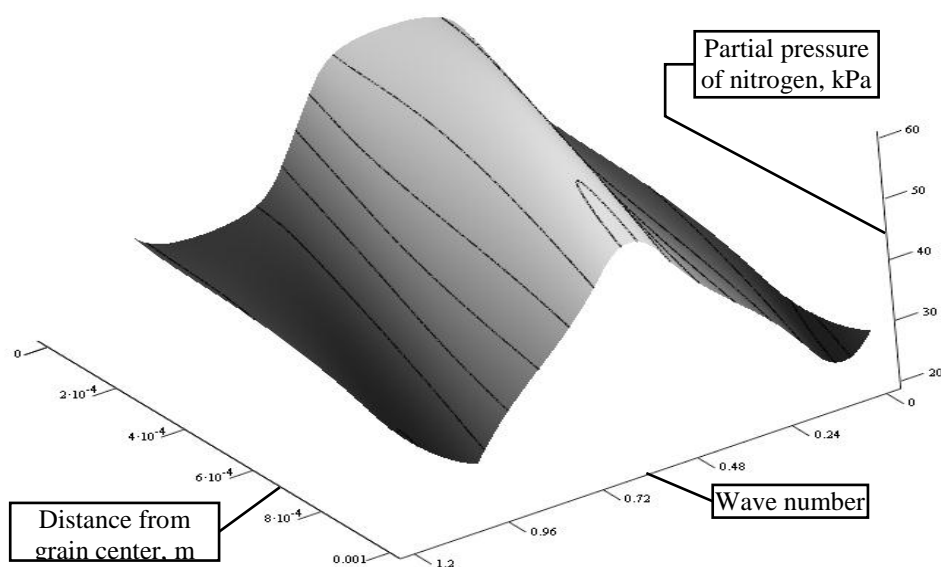
***Figure 3**. The calculated dependence of the partial pressure of nitrogen inside the adsorbent grains during the operation of the adsorption apparatus.*

grains. Conversely, when passing from the adsorption process to the desorption process, the partial pressure of nitrogen in the gas leaving the adsorber becomes smaller than its partial pressure on surface of the grains. It follows that all three curves, if they correctly reflect the physics of the processes that occur, must intersect at the two points.

Since all three curves are calculated according to completely different relationships, the intersection of the three curves at the same point can serve as a marker for estimating the accuracy of the calculations.

Equation (27) makes it possible to calculate the change in the partial pressure of nitrogen inside the grain of adsorbent in the steady-state operating mode of the plant. Figure 3 shows a three-dimensional graph of the variation of the nitrogen partial pressure with respect to the depth of the grain of adsorbent (zeolite).

It can be seen from the graph that the oscillation in the concentration (partial pressure) of nitrogen in the depth of the grain lag behind the phase from oscillations on the surface of this grain, as one would expect.

Smoothing the dependence of the nitrogen concentration on time when immersing deep into the grain of the adsorbent indicates that the high-frequency component of the concentration oscillations penetrates poorly into the interior of the adsorbent grain.

It also follows from the graph that for selected parameters of the facility operation, the partial pressure of nitrogen varies throughout the depth of the zeolite grain.

3. Conclusion

An analytical solution of the system from the differential equations for the diffusion and absorption of a component in adsorbent grains and for material balance of the component for case of harmonic oscillations of the component concentration is obtained.

The technique for calculation of a steady batch periodic adsorption processes based on expansion of a concentration signal into Fourier series of eigenfrequencies of this adsorption process is proposed. After decomposition each of the eigenfrequencies independently of the others is passed through the adsorbent layer, and at the output from this layer all this solutions for the individual eigenfrequencies are summed. The solution of the problem of passing an arbitrary periodic concentration signal through the adsorbent layer is obtained as a result of summing solutions for individual eigenfrequencies.

On a specific example of the adsorption of nitrogen in a layer of zeolite grains with a characteristic size of 2 mm shown the possibility of practical application of the proposed method for calculating periodic adsorption and desorption of gases.

The proposed method can be used to calculate the installations for separation and purification of gases, for example, such as plants operating using the pressure swing adsorption method.

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