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CONCEPTUALLY NEW MODEL OF PRESSURE SWING ADSORPTION

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Abstract

The paper describes a new mathematical model of pressure swing adsorption (PSA) in terms of a set of concentration waves passing through an adsorbent bed. The analytical solution for the passage of the concentration eigenwaves through the arbitrary adsorbent bed is derived. This allows analytical solutions to be found for any shaped concentration signal passing through the adsorbent bed. To do this, it is necessary to decompose the input concentration signal into a set of adsorbed layer eigenwaves and obtain a solution for each of the concentration eigenwaves at the exit of that adsorbed layer. Then, all the concentration eigenwave solutions are combined. This is the solution to the problem of passing an arbitrary concentration signal through the adsorbent bed. This approach is suitable for any periodic adsorption process and allows us to take into account the variable concentration of the components at the entrance of the adsorption layer and the non-stationary diffusion in the adsorbent grain. The wave approach to the analysis of periodic adsorption processes explains the effective operation of PSA units. The analysis of the obtained solutions for PSA units designed for the production of oxygen from the air is provided. The conditions necessary for the highly efficient operation of PSA units are formulated. The results are given for different brands of zeolite, allowing the choice of zeolite to be optimized for the given operating conditions.

Key worlds**:** Pressure swing adsorption; PSA; Adsorption; Oxygen; Nitrogen**.**

КОНЦЕПТУАЛЬНО НОВА МОДЕЛЬ КОРОТКОЦИКЛОВОЇ АДСОРБЦІЇ

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Анотація

У статті описано нову математичну модель короткоциклової безнагрівної адсорбції (КБА) у вигляді набору концентраційних хвиль, що проходять через шар адсорбенту. Отримано аналітичне рішення для проходження власних концентраційних хвиль через довільний шар адсорбенту. Це дозволяє знаходити аналітичні рішення для концентраційного сигналу довільної форми, який проходить через адсорбуючий шар. Для цього необхідно розкласти вхідний концентраційний сигнал в набір власних хвиль даного адсорбційного шару та отримати рішення для кожної з власних концентраційних хвиль на виході з цього шару адсорбенту. Далі всі рішення для власних концентраційних хвиль об'єднуються. Це і є рішенням проблеми проходження концентраційного сигналу довільної форми через шар адсорбенту. Такий підхід придатний для розрахунку будь-яких періодичних адсорбційних процесів і дає змогу врахувати змінну концентрацію компонентів на вході в адсорбційний шар і нестаціонарну дифузію всередині зерен адсорбенту. Хвильовий підхід до аналізу періодичних адсорбційних процесів дає пояснення ефективності роботи сучасних установок КБА. В статті наведено аналіз отриманих рішень для установок КБА, призначених для виробництва кисню з повітря. Сформульовано умови, необхідні для високоефективної роботи установок КБА. Наведені результати розрахунків для різних марок цеолітів, що дозволяють оптимізувати вибір цеоліту для заданих умов роботи установки КБА.

Ключові слова: короткоциклова безнагрівна адсорбція; кисень; азот; цеоліт.

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Introduction

Today there are many plants on the market that operate on the principle of Pressure Swing Adsorption (PSA). These units allow the purification and enrichment of various industrial gases such as oxygen, nitrogen, hydrogen and others.

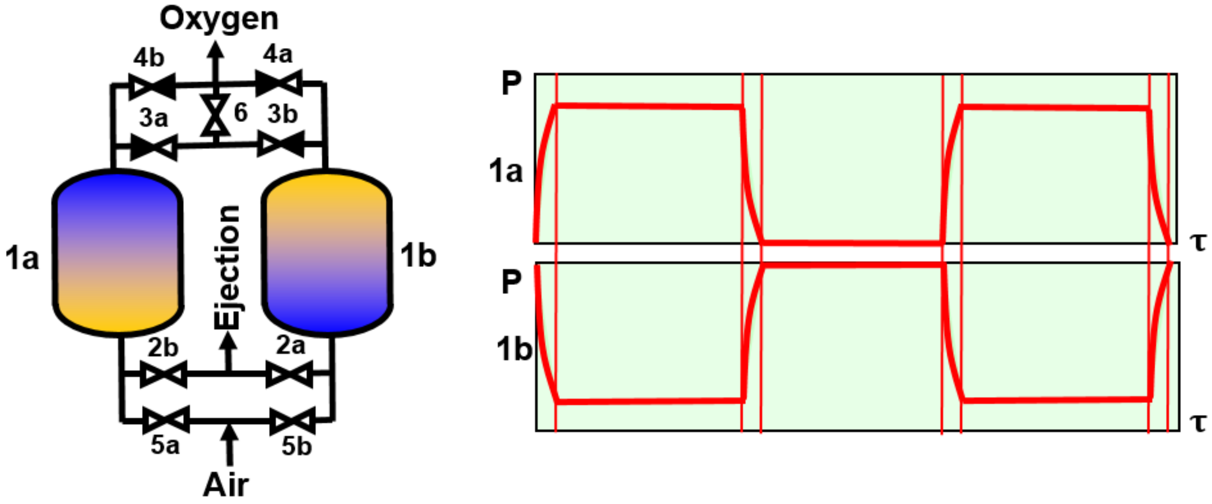

Fig. 1. Scheme and the cycle of the plant for oxygen concentration according to Skarstrom [1].
1 – adsorber; 2,5 – electromagnetic valves; 3,4 – check valves; 6 – throttle;
P – pressure; τ is time

The working principle of all modern PSA units is similar to the working principle of the unit for separation of gas mixtures patented by the American inventor Skarstrom in 1960 [1]. Figure 1 shows the scheme and cycle of the Skarstrom plant.

The main idea of Skarstrom is that part of the production gas is expanded to near atmospheric pressure and used to regenerate the adsorbent. After expansion, the volume of regeneration gas is greater than the volume of compressed gas entering the unit. As a result, the partial pressure of the contaminant being removed from the compressed gas is much lower in the expanded gas. This results in almost complete regeneration of the adsorbent.

Modern plants operating on the PSA principle allow them to obtain high-purity products. For example, in plants for the production of oxygen from the air, it is possible to produce oxygen with a purity of more than 90 % with an extraction ratio of about 40 % [3–6].

It is generally accepted that the operation of PSA units for oxygen production is based only on the difference in the adsorption value of various air components [2–5]. For example, synthetic zeolite 5a, which can be used in plants for oxygen production by the PSA method [3; 7; 8], is about three to five times more active in absorbing nitrogen than oxygen. Strictly speaking, this does not mean that PSA operation is based on this difference. This hypothesis has never been questioned because it is considered quite obvious.

We will perform a simple thought experiment to understand the nature of the problem considered in this paper.

Let's take 1 m^3 of air at an absolute pressure of 6 bar and let it pass through a layer of ideally regenerated zeolite 5a, which is about five times more active at absorbing nitrogen than it is at absorbing oxygen. The equations for the oxygen and nitrogen adsorption isotherms for this zeolite are taken from the reference book [4]. Plots of the changes in the partial pressures of oxygen and nitrogen as a function of the air promotion in the adsorber are shown in Figure 2. It can be seen that the partial pressure of nitrogen decreases faster than that of oxygen. However, nitrogen is approximately four times more abundant in air than oxygen. Therefore, the intersection of the oxygen and nitrogen partial pressure curves, corresponding to a 50 % oxygen concentration, is only reached at an absolute air pressure of approximately 1.75 bar. In other words, to achieve a 50 % oxygen concentration, the adsorbent must absorb approximately 75 % of the initial air. The maximum oxygen concentration that can be obtained at the outlet of such an adsorber at a pressure of 1 bar is about 60 %. In this case, however, the oxygen extraction ratio will be close to zero.

Considering that it will never be possible to completely regenerate the adsorbent by using gas with a nitrogen concentration close to 50 % to regenerate the adsorbent, the partial pressure of nitrogen at the outlet of the adsorber will be even higher in the next cycle. Therefore, it is very problematic to obtain oxygen with a concentration of more than 50 % just because of the difference in adsorption value of oxygen and nitrogen by zeolite 5a.

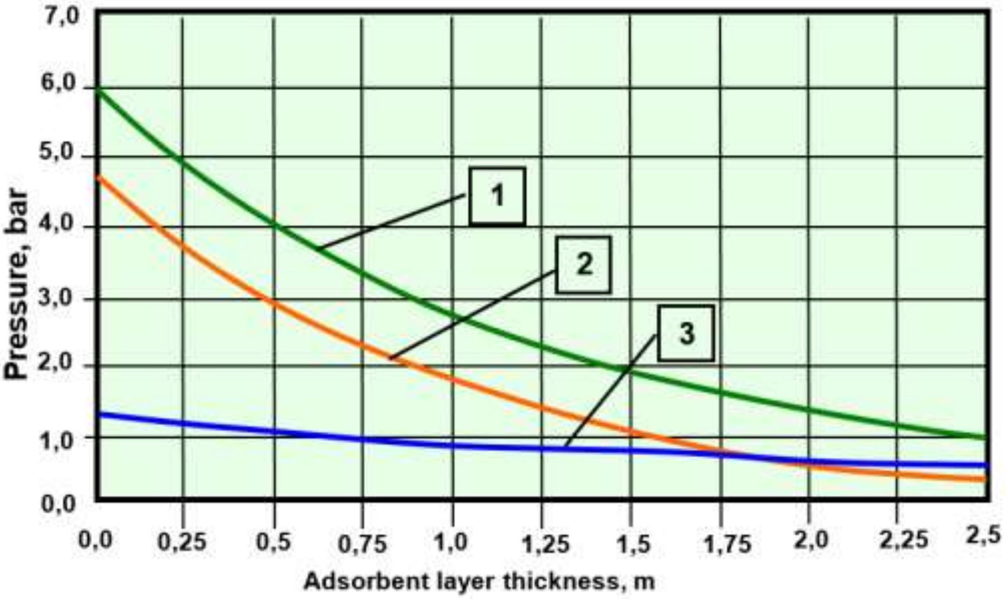

Fig. 2. Absorption of nitrogen and oxygen in a layer of zeolite 5a.
1 is the total pressure of the mixture; 2 – partial pressure of nitrogen;
3 – partial pressure of oxygen

This simple example clearly shows that a difference in oxygen and nitrogen adsorption values is not enough to obtain 90 % oxygen with an extraction ratio of about 40 %.

Companies that produce equipment with such high technical characteristics are not in a hurry to share their calculation methods and experience in developing such equipment with potential competitors. Therefore, they only publish promotional materials that contain a minimum of technical details about the operation of their equipment.

On the other hand, there are dozens of open access scientific publications describing the mathematical model of PSA, which is based on the equations of diffusion of a component in a moving gas [9–12].

Effects that contribute to the high technical performance of the best examples of industrial plants are not mentioned in any of these publications. However, this does not prevent the authors of such publications from declaring a good agreement between the results of the calculations and the available experimental data.

In this work, an attempt has been made to construct a mathematical model of the PSA for the production of oxygen from air, based on the theory of wave adsorption. Such an approach allows to explain the effects responsible for such high technical indicators as modern PSA plants have. In addition, the proposed mathematical model allows the clarification of the adsorbent requirements necessary for the efficient operation of PSA plants.

Wave Mathematical model of a Periodic Adsorption Process

For the analytical description of the sorption kinetics and dynamics we use the wave adsorption model presented in [13–16]. This model allows the calculation of transient adsorption processes with variable gas composition at the inlet of the adsorption apparatus.

In the mathematical description of the adsorption of a gas mixture, as in [13; 14], the following pattern of propagation of a component in a porous adsorbent layer was assumed.

The component of interest is assumed to be dissolved in a non-adsorbable carrier gas. The carrier gas is filtered through the adsorbent layer at a constant rate. The assumption that there is no longitudinal gas mixing in the adsorber is equivalent to the use of a carrier gas in the considered model. Moreover, the carrier gas moving at a constant velocity plays the role of a moving reference system, relative to which the phase shift of the component concentration fluctuations is determined. Thus, the carrier gas is an abstract element in the considered mathematical model and is not necessary for the implementation of the model.

Near the contact points of the adsorbent grains, stagnant zones are formed where the gas is practically immobile. The main flow of the carrier gas with the dissolved component passes through a chain of cavities and voids in the space between the grains of the adsorbent. Therefore, the entire space in which the adsorbent is located is divided into two parts: a fixed frame of adsorbent grains with adjacent stagnation zones, and a system of interconnected voids and channels in which the carrier gas moves.

In the fixed frame, molecular diffusion in the carrier gas is the main mode of transport for the component of interest.

In the system of channels between the grains of the adsorbent, the transport of the component of interest is mainly by convection.

The proposed formulation of the problem considers the removal of the component from the stationary frame to the moving carrier gas as the sink of the component. A separate equation of the component material balance describes the convection of a component in channels with a moving carrier gas.

Considering the above, the first equation of molecular diffusion in a fixed frame can be written as:

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

where $C(x,y,\tau)$ is the actual volume concentration of the component in the fixed frame, [m^3/m^3]; $Cg(x,\tau)$ is the actual volume concentration of the component in the carrier gas, [m^3/m^3]; β is the mass transfer coefficient between the gas in the fixed frame and the gas moving in the cavities between the adsorbent grains, [$m^3/(s \cdot m^2)$]; F is the specific surface area of the fixed frame, [m^2/m^3]. D_E is the equivalent value of the sorbate diffusion coefficient in the adsorbent grain, taking into account: 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 Henry constant for the adsorption of the component, where a is an adsorption of that component, expressed in cubic meters of sorbate per 1 m^3 of bulk volume of adsorbent.

Henry's constant is present in the reported differential equation for the diffusion of a component in a fixed framework. This means that the proposed mathematical model assumes a linear model of gas adsorption on the adsorbent. The adsorption isotherm corresponding to this model is called Henry's isotherm. If any other dependence is chosen to describe the adsorption of the component, we obtain a non-linear equation for the diffusion of the component in the fixed framework. This equation is either not analytically solvable or its solution is too complicated.

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

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

where G is the volumetric flow rate of the carrier gas and component assigned to the unit area of the adsorbent bed, [m^3/s]; δ is the characteristic particle size in the adsorbent bed, [m].

By combining these two equations, we can determine the distribution of the concentration of the component in the moving carrier gas and in the fixed frame.

It solves the problem of diffusion and adsorption of the component in a layer of the adsorbent through which a carrier gas flows.

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

The solution of the resulting system is analogous to the solution of the system described in [13–16].

Equation (1), after the transition to the operator form with respect to time, takes the form:

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

where s is the time differentiation operator [17]; $Co(x,y)$ is the initial distribution of the component concentration in the adsorbing layer. For simplicity, we will also have the assumption that the initial distribution of the component concentration is zero.

We apply the finite Fourier integral transformation to the coordinate x, choosing the cosine function as the kernel of the transformation [18–20]:

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

Selecting this form of the finite Fourier integral kernel automatically provides second-order zero boundary conditions at the ends of the fixed frame (adsorbent layer).

After performing the finite Fourier transform with respect to coordinate *x*, equation (1) becomes:

$$-\frac{(2\pi\cdot k)^2}{h^2}\overline{\overline{C}}_k(y,s)+\frac{\partial^2\overline{\overline{C}}_k(y,s)}{\partial y^2}=\left(\frac{K_G}{D_E}\cdot s\right)\cdot\overline{\overline{C}}_k(y,s)+\frac{\beta\cdot F}{D_E}\left[\overline{\overline{C}}_k(y,s)-\overline{\overline{Cg}}_k(s)\right]. \tag{5}$$

We perform the finite Fourier integral transformation with respect to the *y*-coordinate. We use the transformation kernel, which has the form:

$$\overline{\overline{C}}_{k,n}(s)=\int_0^\delta\overline{\overline{C}}_k(y,s)\cos\left(\mu_n\frac{y}{\delta}\right)dy;\quad n=0,1,2\ldots \tag{6}$$

We find the eigenvalues of the finite Fourier transform μn to ensure that the third order boundary condition is satisfied at the free surface of the grains and the second order zero boundary condition is satisfied at the grain symmetry axis.

To find the eigenvalues of the finite Fourier transform, we use the transcendental equation:

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

The diffusion equation in the fixed frame after the cosine Fourier integral transformation along the coordinate *y* becomes:

$$-\frac{(2\pi\cdot k)^2}{h^2}\overline{\overline{C}}_{k,n}(s)-\frac{\mu_n^{\,2}}{\delta^2}\overline{\overline{C}}_{k,n}(s)=\left(\frac{K_G}{D_E}\cdot s\right)\cdot\overline{\overline{C}}_{k,n}(s)+\frac{\beta\cdot F}{D_E}\left[\overline{\overline{C}}_{k,n}(s)-\overline{\overline{Cg}}_k(s)\frac{\mu_n}{\delta}\sin(\mu_n)\right]. \tag{8}$$

From this, we get the image of a function that describes the concentration of the component in the fixed frame:

$$\overline{\overline{C}}_{k,n}(s)=\frac{\overline{\overline{Cg}}_k(s)\dfrac{\beta\cdot F}{D_E}\dfrac{\mu_n}{\delta}\sin(\mu_n)}{\left(\left(\dfrac{(2\pi\cdot k)^2}{h^2}+\dfrac{\mu_n^{\,2}}{\delta^2}+\dfrac{\beta\cdot F}{D_E}\right)+\dfrac{K_G}{D_E}\cdot s\right)}. \tag{9}$$

This equation allows us to solve the fixed frame diffusion equation in the form of a double Fourier series:

$$C(x,y,s)=\frac{2}{h}\frac{\beta\cdot F}{D_E}\sum_n\left\{\frac{\mu_n}{\delta}\sin(\mu_n)\frac{2}{\delta}\cos\left(\mu_n\frac{y}{\delta}\right)\sum_k\frac{\overline{\overline{Cg}}_k(s)\cdot\cos\left(2\pi\cdot k\dfrac{x}{h}\right)}{\left(\dfrac{(2\pi\cdot k)^2}{h^2}+\dfrac{\mu_n^{\,2}}{\delta^2}+\dfrac{K_G}{D_E}\cdot s+\dfrac{\beta\cdot F}{D_E}\right)}\right\}. \tag{10}$$

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

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

Until now, the method of finite integral transformations described in the scientific literature [19] was used to solve the diffusion equation of a component in a fixed frame.

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

Eigenfrequencies are frequencies at which an integer number of concentration waves propagate along the thickness of the adsorption layer:

$$Cg(x,\tau) = A_k \cos\left(2\pi \cdot k\left(\frac{x}{h}+\frac{\tau}{T}\right)\right) = A_k\left[\cos\left(2\pi \cdot k\frac{x}{h}\right)\cos\left(2\pi \cdot k\frac{\tau}{T}\right) - \sin\left(2\pi \cdot k\frac{x}{h}\right)\sin\left(2\pi \cdot k\frac{\tau}{T}\right)\right]. \qquad (12)$$

where T is the period of eigen oscillations of the component concentration, [s]; A_k is the amplitude of the concentration oscillations of the component in the carrier gas moving inside the adsorbent [m^3/m^3].

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

$$\overline{\overline{Cg}}_m(\tau) = \int_0^h Cg(x,\tau)\cos\left(2\pi \cdot m\frac{x}{h}\right)dx = A_k \cos\left(2\pi \cdot k\frac{\tau}{T}\right)\int_0^h \cos\left(2\pi \cdot k\frac{x}{h}\right)\cos\left(2\pi \cdot m\frac{x}{h}\right)dx -$$
$$- A_k \sin\left(\pi \cdot k\frac{\tau}{T}\right)\int_0^h \cos\left(2\pi \cdot k\frac{x}{h}\right)\sin\left(2\pi \cdot m\frac{x}{h}\right)dx \qquad (13)$$

To find the integrals, we use the mutual orthogonality of concentration eigenwaves, given by the equation:

$$\int_0^h \cos\left(2\pi k\frac{x}{h}\right)\cos\left(2\pi m\frac{x}{h}\right)dx = \frac{h}{2}, \_if\,\{m=k\}$$
$$\int_0^h \cos\left(2\pi k\frac{x}{h}\right)\sin\left(2\pi m\frac{x}{h}\right)dx = 0, \_if\,\{m \neq k\} \qquad (14)$$

With this in mind:

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

We move to the time differentiation operator form:

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

The meaning of the last transformation is that all but one of the coefficients of the Fourier series will be zero if a concentration signal is applied in the form of a harmonic wave whose frequency matches one of the eigen frequencies of the adsorption layer to which this concentration signal is applied. The solution of the diffusion equation in this case can be represented as a relatively simple finite expression instead of a general infinite Fourier series.

As is well known from the theory of oscillations, when a system is forced to oscillate, the frequency of these oscillations will always coincide with the frequency of the external action that caused the oscillations. Therefore, the frequency of the concentration oscillations inside the adsorbent grain will be the same as the frequency of the concentration oscillations penetrating the adsorbent bed from the outside. In our case, this will be one of the eigen frequencies of the adsorbing layer.

In this case, the length of the concentration wave propagating in the adsorbent grain is generally different from the length of the concentration wave propagating in the adsorbent layer under consideration.

Let us consider a concrete example of adsorption of nitrogen from air using zeolite. For the calculation of pressure swing adsorption plants designed for the production of oxygen, it is necessary to solve such problems.

In this case, the equivalent diffusion coefficient of nitrogen in the zeolite granules is of the order of $D_E \approx 10^{-5}$ m^2/s, and the product of the mass transfer coefficient and the adsorbent grain surface area $\beta F \approx 10$ m^3/s. Therefore, the parameter $\beta F/D_E$, when the nitrogen is absorbed by the zeolite, has values in the order of 10^6 m. The corresponding values μ_n found by formula (7) are very close to $(\pi + n\pi/2)$, where n is an integer.

This means that an integer number of concentration waves can almost fit into the grain of the adsorbent. Therefore, we can use the selection rule (14) to simplify the solution for the coordinate y. However, it must be noted that in this case the selection rule is only an approximation. Therefore, the sum of the infinite Fourier series may deviate significantly from the approximation obtained in this way, even if the Fourier series term deviation is relatively small.

In this case, 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 for the *y*-coordinate can be found using the norm of the *n*-th harmonic, whose square is equal to:

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

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

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

$$\overline{\overline{C}}_{k,n}(s) = \frac{\dfrac{A_k h}{2}\dfrac{\beta F}{D_E}}{\left(\left(\dfrac{(2\pi\cdot k)^2}{h^2} + \dfrac{\mu_n{}^2}{\delta^2} + \dfrac{\beta F}{D_E}\right) + \dfrac{K_G}{D_E}\cdot s\right)} \times \frac{\dfrac{\mu_n}{\delta}\sin(\mu_n)\cdot\left\|\psi_y\right\|_n^2\cdot s}{\left(s^2 + \left(\dfrac{2\pi\cdot k}{T}\right)^2\right)} . \qquad (18)$$

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

$$-\frac{\dfrac{A_k h}{2}\dfrac{\beta F}{D_E}}{\left(\left(\dfrac{(2\pi\cdot k)^2}{h^2} + \dfrac{\mu_n{}^2}{\delta^2} + \dfrac{\beta F}{D_E}\right)\cdot\dfrac{D_E}{K_G} + s\right)} \times \frac{\dfrac{\mu_n}{\delta}\sin(\mu_n)\cdot\left\|\psi_y\right\|_n^2\cdot\left(\dfrac{(2\pi\cdot k)^2}{h^2} + \dfrac{\mu_n{}^2}{\delta^2} + \dfrac{\beta F}{D_э}\right)}{\left(\left(\dfrac{(2\pi\cdot k)^2}{h^2} + \dfrac{\mu_n{}^2}{\delta^2} + \dfrac{\beta F}{D_E}\right)^2 + \left(\dfrac{K_G}{D_E}\right)^2\cdot\left(\dfrac{2\pi\cdot k}{T}\right)^2\right)} . \qquad (19)$$

An inverse exponential function of time is the original of this expression. At steady state, this term tends to zero. Therefore, this term is omitted in the following, since the problem is one of steady-state adsorption.

The second term can be rewritten as:

$$\overline{\overline{C}}_{k,n}(s) = \frac{\dfrac{A_k h}{2}\dfrac{\beta F}{D_E}\dfrac{\mu_n}{\delta}\sin(\mu_n)\cdot\left\|\psi_y\right\|_n^2}{\left(\left(\dfrac{(2\pi k)^2}{h^2} + \dfrac{\mu_n{}^2}{\delta^2} + \dfrac{\beta F}{D_E}\right)^2 + \left(\dfrac{K_G}{D_E}\right)^2\left(\dfrac{2\pi k}{T}\right)^2\right)} \left\{\frac{\left(\dfrac{K_G}{D_E}\right)\left(\dfrac{2\pi k}{T_k}\right)^2}{\left(s^2 + \left(\dfrac{2\pi k}{T}\right)^2\right)} + \frac{\left(\dfrac{(2\pi k)^2}{h^2} + \dfrac{\mu_n{}^2}{\delta^2} + \dfrac{\beta F}{D_E}\right)s}{\left(s^2 + \left(\dfrac{2\pi k}{T}\right)^2\right)}\right\} . \qquad (20)$$

We go to the original of this expression at time. To make it easier to write, let us introduce the following multi-indexed notation:

$$Ba_{k,n} = \frac{\dfrac{A_k h}{2}\dfrac{\beta F}{D_E}\dfrac{\mu_n}{\delta}\sin(\mu_n)}{\left[\left(\dfrac{(2\pi\cdot k)^2}{h^2} + \dfrac{\mu_n{}^2}{\delta^2} + \dfrac{\beta F}{D_E}\right)^2 + \left(\dfrac{K_G}{D_E}\right)^2\left(\dfrac{2\pi\cdot k}{T}\right)^2\right]} ; \qquad (21)$$

$$Bc_{k,n} = \left(\frac{(2\pi\cdot k)^2}{h^2} + \frac{\mu_n{}^2}{\delta^2} + \frac{\beta\cdot F}{D_E}\right) ; \qquad (22)$$

$$Bs_k = \left(\frac{K_G}{D_E}\right)\cdot\left(\frac{2\pi\cdot k}{T}\right) . \qquad (23)$$

Then

$$\overline{\overline{C}}_{k,n}(\tau) = Ba_{k,n}\sqrt{\left(Bc_{k,n}\right)^2 + \left(Bs_{k,n}\right)^2}\cdot\left\|\psi_y\right\|_n^2\cdot\cos\left(\left(\frac{2\pi k}{T}\right)\tau - \varphi_{k,n}\right)\cos\left(\mu_n\frac{y}{\delta}\right) , \qquad (24)$$

Were

$$\varphi_{k,n} = \arccos\left(\frac{Bc_{k,n}}{\sqrt{(Bc_{k,n})^2+(Bs_k)^2}}\right) = \arcsin\left(\frac{Bs_k}{\sqrt{(Bc_{k,n})^2+(Bs_k)^2}}\right) = \arctan\left(\frac{Bs_{k,n}}{Bc_{k,n}}\right). \tag{25}$$

The physical meaning of this formula is clear: the amplitude of the concentration fluctuations in the stationary frame is proportional to the amplitude of the concentration fluctuations in the carrier gas (at the entrance to the adsorbent bed) multiplied by a specific coefficient depending on the gas velocity and the adsorbent properties.

The phase of the concentration oscillations in the stationary frame lags behind the phase of the concentration oscillations in the carrier gas entering the adsorbent bed.

Unlike sound or electromagnetic waves, concentration waves are not reflected from the edges of the adsorbent bed. With this in mind, the expression that describes the change in the concentration of the component in the fixed frame is as follows:

$$C_k(x,y,\tau) = \frac{2}{h} Ba_{k,n}\sqrt{(Bc_{k,n})^2+(Bs_k)^2}\cdot\left\|\psi_y\right\|_n^2\cdot\cos\left(2\pi k\left(\frac{\tau}{T}+\frac{x}{h}\right)-\varphi_k-\mu_k\frac{y}{\delta}\right). \tag{26}$$

When a whole number of waves are placed in the adsorbent grain, the scaling factor value is equal to the following equation:

$$\left\|\psi_y\right\|_n^2 = \frac{\delta}{2}.$$

With this in mind, we have:

$$C_k(x,y,\tau) = \frac{2}{h} Ba_{k,n}\sqrt{(Bc_{k,n})^2+(Bs_k)^2}\,\frac{\delta}{2}\cos\left(2\pi\cdot k\left(\frac{\tau}{T}+\frac{x}{h}\right)-\varphi_k-\mu_k\frac{y}{\delta}\right). \tag{27}$$

The finite particle size of the adsorbing material is reflected in an additional phase shift of the concentration wave in the adsorbing particles and the adsorbing layer.

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

Taking into account the fact that the accepted mathematical model considers only such oscillations of the component concentration where the phases at the input and output are equal, we construct the cosine Fourier transform for the coordinate *x*:

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

$$+\frac{2\pi\cdot k}{h}\int_0^h Cg(x,\tau)\sin\left(2\pi\cdot k\frac{x}{h}\right)dx = Cg(h,\tau)-Cg(o,\tau)+\frac{2\pi\cdot k}{h}\overline{\overline{Cg}}{}_k^S(\tau);\quad k=0,1,2\ldots \tag{28}$$

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

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

As in the work of the author [14], it is assumed that in the steady state regime the mass of the adsorbed component in the concentration wave passing through the adsorbent layer remains unchanged. This is possible only if the length of an integral number of concentration waves in the adsorbed layer is equal to the thickness of this layer. Therefore, for the eigenwaves at the entrance and exit of this adsorbed layer, the difference between the instantaneous concentrations of the component in the carrier gas is zero:

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

From this:

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

It follows from this equation that if a cosine concentration wave is propagating in the fixed frame, it will produce a sine concentration wave of a certain amplitude in the carrier gas. This can be regarded as the spatial delay of the concentration wave in the carrier gas with respect to the concentration wave in the fixed frame.

During the stationary motion of a concentration wave, multiple exchanges of components take place between the carrier gas and the adsorbent. As a result, the amplitudes of the mass oscillations of the components in the carrier gas and in the adsorbent are identical.

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

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

The amplitudes of concentration waves cannot be added during interference, unlike the amplitudes of sound or electromagnetic waves. This is because increasing the concentration of a component without expending energy violates the second law of thermodynamics.

When two streams are mixed, the resulting concentration of the component is found as the weighted average of the concentrations of the component in the mixed streams. Similarly, in the case of superposition of concentration waves, the amplitude of the resulting wave is the average of the amplitudes of the interfering concentration waves. To implementation of this condition in the case of interference of concentration waves, it is sufficient to assume that the amplitude of the concentration wave at the exit from the adsorption layer is equal to half of the amplitude of the concentration wave at the entrance to this adsorption layer.

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

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

Given this, we obtain a relatively simple solution for the concentration eigenwaves at the outlet of the adsorptive layer:

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

The physical sense of this formula is obvious: for eigenwaves propagating through the adsorbent bed, the frequency remains the same and the wave phase is delayed in time by the angle $\varphi_k+\mu_n$ and in space by the angle ω_k. Different concentration waves also have different phase angles.

Equations (30) and (32) are derived in a different way in the work of the author [16]. The derivation of these equations in different ways confirms their correctness.

Since any periodic concentration signal can be represented as a sum of harmonic oscillations, we can easily obtain a solution for any process of periodic operation of the adsorption apparatus in an unsteady but stationary regime by means of a relatively simple solution for the eigenwaves of the adsorption layer.

Using the Wave Adsorption Method to Calculate a Periodic Adsorption Process

We demonstrate the potential of the obtained solutions for the calculation of a pressure swing adsorption process.

Consider the periodic process of nitrogen adsorption in a layer of zeolite grains of predetermined size. Such a process is crucial for plants 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 at an overpressure of 0.8 bar. The adsorbent is regenerated under vacuum. The operating time of the apparatus in nitrogen uptake mode and the regeneration time of the adsorbent are assumed to be the same. The volumetric flow rate of the air supplied to the adsorber and the pumping speed (volumetric flow rate) of the vacuum pump is assumed to be equal. The low pressure limit of the vacuum pump should be less than 0.2 bar.

Calculations are performed for an adsorption layer of 1 m height. The operating time of the adsorption apparatus in the absorption regime is assumed to be 100 s.

The air velocity in the adsorbent bed is assumed to be constant and equal to 0.1 m/s. The grain size of the adsorbent is assumed to be 2 mm. The dimensionless Henry constant for the absorption of nitrogen by zeolite 5a is assumed to be K_G=11.7, and the equivalent diffusion coefficient is assumed to be $2.4 \cdot 10^{-6}$ m^2/s.

The coefficient of mass transfer from the grains of the adsorbent to the carrier gas has been determined from the formulas given in the literature [4].

The flexibility of the proposed method can be illustrated by the example of the assumption of a linear change of the pressure during the entry and the exit of the gas from the adsorber. The duration of the inlet and outlet processes is assumed to be equal to 15 % of the operating time of the adsorber.

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

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

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

Then, using formulas (27) and (33), we find Fourier series terms for the concentration of nitrogen in the fixed frame and for the concentration of nitrogen in the carrier gas exiting the adsorber.

In this example, calculations were performed on the first hundred terms of a Fourier series. This eliminates the oscillations that are usually present in the calculation plots when a Fourier series is finite.

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

The shape of the obtained graphs corresponds to the ideas about the physical processes taking place in the adsorber. At the stage of nitrogen adsorption, its partial pressure at the outlet of the adsorber increases due to saturation of the adsorbent. At this stage, the nitrogen partial pressure is slightly higher than the nitrogen partial pressure at the surface of the adsorbent grains. During regeneration of the adsorbent, the picture is reversed, the nitrogen partial pressure at the outlet of the adsorber decreases, and throughout the regeneration period, the nitrogen pressure in the carrier gas remains lower than the pressure at the surface of the adsorbent.

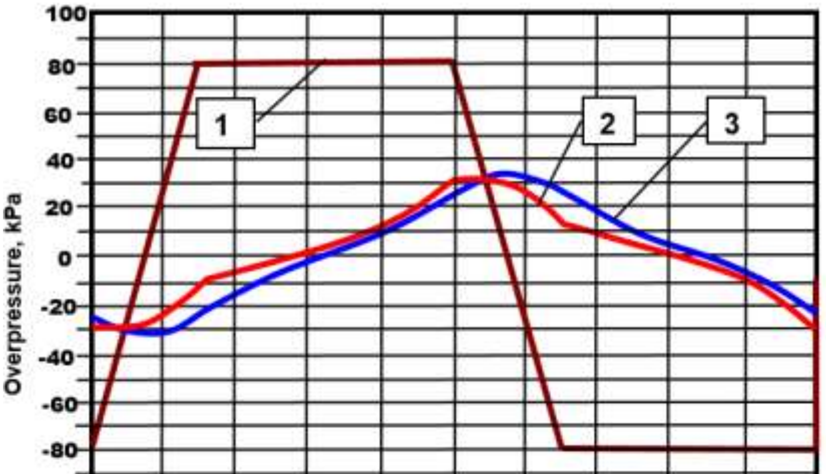

Fig. 3. Calculated dependences of the excess partial pressure of nitrogen.
1 - at the inlet to the adsorber, taking into account the periods of gas inlet and outlet;
2 - on the surface of adsorbent grains; 3 in the carrier gas exiting the adsorber

The fact that there are two points where all three curves intersect is an interesting feature of this graph. This feature reflects the physics of the processes taking place in the apparatus.

When the desorption of nitrogen ends and the adsorption process begins, the direction of movement of the nitrogen changes. The partial pressure of nitrogen entering the adsorber will be higher than the pressure of nitrogen on the surface of the adsorbent grains. As a result, the partial pressure of nitrogen in the gas leaving the adsorber will also be higher than the pressure on the surface of the adsorbent grains. Conversely, in the transition from adsorption to desorption, the nitrogen partial pressure in the gas leaving the adsorber becomes lower than its partial pressure on the surface of the granules. It follows that all three curves must intersect at these two points if they are to correctly reflect the physics of the processes occurring.

The intersection of the three curves at the same point can be used as a marker to estimate the accuracy of the calculations, since all three curves are calculated according to completely different relationships.

Wave Adsorption Model of pressure swing adsorption

In this paper, we consider a steady-state periodic adsorption process. Therefore, the gas flow at the inlet of each adsorber of the PSA unit can be represented as a concentration signal with an infinite number of periodic repetitions. It is well known from mathematical analysis that any periodic process can be represented as the sum of an infinite series of harmonic oscillations. Therefore, it is possible to expand the concentration signal entering the adsorber into a Fourier series in terms of the eigenfrequencies of the given adsorption apparatus, if the shape of the concentration signal is known. The eigenfrequencies of the adsorption apparatus are those concentration wave frequencies at which an integer number of waves fit along the length of the adsorber.

An analytical solution to the problem of passing a periodic concentration signal of any shape through the adsorber is obtained by summing the analytical solutions obtained for individual concentration waves at the exit of the adsorber.

However, this is not sufficient to construct a mathematical model of the PSA unit because the gas flow in the adsorber of the PSA unit moves alternately in one direction and then in the other. This problem can be solved by using the linearity of the system of equations (1) and (2).

As you know, if there are two particular solutions to a system of linear homogeneous differential equations, then the sum or difference of these solutions will also solve the system of differential equations. Therefore, to construct a mathematical model of the PSA unit, it is possible to combine the solution for the direct flow of the mixture to be separated with the solution for the regenerating gas flow moving in the opposite direction.

Since the sum and the difference of the solutions of the problem for the direct flow of the mixture to be separated and the problem for the flow of the regenerating gas are equal from a mathematical point of view, this means that the system of differential equations (1) and (2) with the alternating forward and reverse gas flow has two solutions. Which of these solutions is implemented in practice depends on the initial conditions.

The PSA unit is a complex self-oscillating system with non-stationary processes and flows. Therefore, modeling and calculations of such units should be performed on the basis of the conceptual apparatus and methods of the theory of dynamical systems.

In terms of the theory of dynamical systems, the steady-state operation of the PSA unit with repeated fluctuations of the concentrations and pressures of the components is commonly called the limit cycle. Different starting modes of the PSA unit, in which the concentrations and pressures of the components of the gas mixture are not equal, but in the limit, lead to the same steady-state operation of the unit, its limit cycle.

In the theory of dynamical systems, objects are also known to have multiple limit cycles. The initial conditions under which the system can enter multiple limit cycles are called bifurcation points.

Consequently, the adsorber of the PSA unit, through which the gas mixture with the adsorbed component and the countercurrent flow of the regenerating gas pass alternately, has two stationary operating modes or two limit cycles in the terminology of the theory of dynamical systems.

The first limit cycle is reached when, at the start of the PSA unit, the adsorbent is regenerated according to the absorbed component. In this case, as the gas mixture passes through the adsorber, the dissolved component is actively adsorbed and almost pure carrier gas comes out of the adsorber. The regenerating gas will carry the component absorbed by the adsorbent out of the adsorber, thereby regenerating the adsorbent. As a result, the absorbed component will virtually not pass through the PSA unit.

The second stable operating mode of the PSA unit is realized when the adsorbent is saturated with the absorbed component at the time of start-up. In this case, when the carrier gas with the dissolved component passes through the adsorber, the component will practically not be absorbed by the adsorber because it is already saturated with the component. Therefore, the carrier gas will leave the PSA unit with virtually the same amount of absorbed component as when it entered the unit. If such a gas is used to regenerate the adsorber, the content of the component in the adsorber will also remain virtually unchanged. As a result, in this mode, the absorbed component will easily pass through the structure of the PSA unit.

It should be noted that both operating modes described can be implemented on the same unit with the same adsorbent. The transition from one stable state to the other will occur when a certain degree of saturation of the adsorbent is reached at the time of the start-up of the unit. This degree of saturation of the adsorbent with the absorbed component, in terms of dynamic systems theory, will be the bifurcation point from which, as a result of insignificant deviations, one of the two stable system states can be reached.

If the atmospheric air is considered as a mixture of two components: nitrogen and oxygen, then to simulate, for example, a PSA plant designed to produce oxygen, it is necessary to consider separately the processes of absorption of oxygen and nitrogen by the adsorbent. In this case, there are not two, but four variants of initial conditions.

The first mode is the simplest from the analytical point of view if at the beginning of the plant operation, the adsorbent is completely regenerated in terms of both oxygen and nitrogen. This case is discussed in detail above, in the introduction to the article. In this mode, the oxygen concentration at the outlet of the unit is determined by the difference in the adsorption value of the components of the mixture fed to the inlet of the adsorber. For example, if nitrogen is absorbed several times more actively than oxygen, the outlet of the unit will be air enriched with oxygen to a concentration of 50-60%.

This, but not the low selectivity of the adsorbents used, seems to explain the low efficiency of the first PSA units for oxygen production [1, 3].

The second possible mode of operation of the PSA plant for oxygen production is when the plant starts working with an adsorber fully saturated with nitrogen and oxygen. In this case, as in the previous case, the oxygen concentration at the outlet of the adsorber is determined by the difference in adsorption of the components of the mixture to be separated. It is easy to see that if the isotherms of nitrogen and oxygen adsorption are linear or close to linear, the same low oxygen concentration will be obtained in the first and in the second mode of operation of the PSA units. Therefore, both cases are of no practical interest.

The third mode of operation of the PSA unit is obtained when the adsorbent is saturated with oxygen and regenerated with nitrogen at start-up. In this case, nitrogen is actively absorbed from the air entering the adsorber and almost all of the oxygen passes through the adsorber. As a result, almost pure oxygen will come out of the adsorber. If some of this gas is used to regenerate the adsorber, even after expansion to near atmospheric pressure, the partial pressure of oxygen in the regenerating gas will also be quite high. For example, if the pressure of the air entering the separation unit is 5 bar, then the partial pressure of oxygen in this air will be about 1 bar, so the degree of saturation of the adsorber will not change much during the operation of the unit. Therefore, a necessary condition for achieving high values of the oxygen recovery factor is almost complete saturation of the adsorbent with oxygen during operation of the PSA unit.

The situation is different for nitrogen. Since the regeneration gas contains little nitrogen, the adsorbed nitrogen is effectively removed from the adsorbent.

It is obvious that in this mode of operation of the PSA unit it is possible to obtain practically pure oxygen in a relatively large amount.

If the adsorbers are filled with oxygen during the installation, then such a unit will very quickly enter the mode of obtaining almost pure oxygen after the start-up.

And finally, the fourth case, when the PSA unit starts working with an adsorbent saturated with nitrogen and regenerated with oxygen. As shown in the previous case, it can be concluded that the output of such a plant will be practically pure nitrogen. Moreover, it is not at all necessary that the adsorption of oxygen by the adsorbent used in the plant be greater than the adsorption of nitrogen.

The question remains why in PSA air separation almost all argon is found together with oxygen, although the adsorbent is not specifically enriched and regenerated with argon.

This is explained by the fact that argon adsorbs on the same active sites of the adsorbent surface as oxygen and therefore competes with oxygen for these active sites. As a result, as the adsorbent becomes saturated with oxygen, the adsorption of argon by that adsorbent will decrease. In other words, saturating the adsorber with oxygen is equivalent to saturating it with argon. Therefore, if oxygen can pass through the adsorber almost unhindered, then argon will easily pass through the same adsorber. Conversely, if the adsorber absorbs oxygen, it will actively absorb argon.

It follows that the necessary condition for the efficient operation of the PSA device is the adsorption of the components of the mixture to be separated at different active centers of the adsorber surface.

An external manifestation of this is the independence of the adsorption of a component from the degree of saturation with other components of the mixture. In fact, the separation of the gas mixture in PSA units takes place in the process of adsorption of the molecules of the gases to be separated on different active sites on the surface of the adsorbent.

On the other hand, as shown in the example discussed in the introduction, even a significant difference in the binding energy of the molecules of the adsorbed gases to the surface of the adsorbent, which appears externally as a difference in the absolute value of adsorption of gases to this adsorbent, does not ensure effective separation of the gas.

Results of PSA unit calculations using the Wave Adsorption Model

Calculations of the PSA plant for oxygen production were performed. The adsorbents 5a, OxySiv 5 and OxySiv 7 were selected for the wave adsorption model calculation. The last two zeolites were developed at the Linde Air Products Division Laboratory specifically for use in the oxygen production adsorption unit. The adsorption isotherms for these zeolites were taken from the reference book [4] for 5a and [21–24] for Oxysiv 5 and Oxysiv 7. Figure 4 shows the adsorption isotherms of nitrogen and oxygen for the zeolites 5a, Oxysiv 5 and Oxysiv 7.

In all calculations, the length of the adsorber is assumed to be 0.5 m, the operating time of the unit is assumed to be 60 s, and the characteristic size of the adsorbent grain is assumed to be 1 mm. A mixture of nitrogen and oxygen under the absolute pressure of 7 bar and with the oxygen concentration of 21 % is supplied to the inlet of the unit. All other parameters of the plant: gas velocity in the adsorbers, bulk weight of the adsorbent, temperature of the adsorbent, etc. are assumed to be the same.

In order to simplify the analysis and interpretation of the results of the calculations in the mathematical model, the gas overflow between the adsorbers during the changeover has not been taken into account. If necessary, the gas overflow between the adsorbers can be easily taken into account by setting the time of this operation.

Figure 4 shows the calculated graphs of the dependence of the oxygen concentration at the outlet of the device on the oxygen extraction ratio.

First of all, it should be noted that the above mathematical model allows us to explain the mechanisms by which the oxygen concentration exceeds 90 % with an extraction ratio greater than 30 %. Using the 5a zeolite, an oxygen concentration of 80 % was obtained with an extraction ratio of 35 %. This significantly exceeds the result of a simple absorption of oxygen and nitrogen with a fully refined adsorbent considered in the introduction.

It should be noted once again that these indicators are obtained without taking into account the leveling pressure stage in the adsorbers when changing them. It is quite obvious that by taking into account the leveling of the gas pressure when changing the adsorbers, the oxygen extraction ratio from the air will increase. This conclusion is also confirmed experimentally.

The review [25] refers to the results of a study of PSA plants for oxygen production, according to which the pressure equalization stage allows to reduce the energy consumption for oxygen. Therefore, taking into account the pressure equalization stage in the adsorbers, the calculated indicators of the plants will be even better, i.e. they will become approximately the same as in industrial samples of PSA plants. Similar results are presented in [26–29].

Calculations also show that adsorbents with a higher nitrogen to oxygen adsorption ratio are not necessarily the best for PSA plants. In the example considered, the 5a zeolite adsorbs more nitrogen and oxygen than the OxySiv 5 zeolite, but the OxySiv 5 zeolite provides a significantly higher oxygen concentration than the 5a zeolite in the selected installation mode.

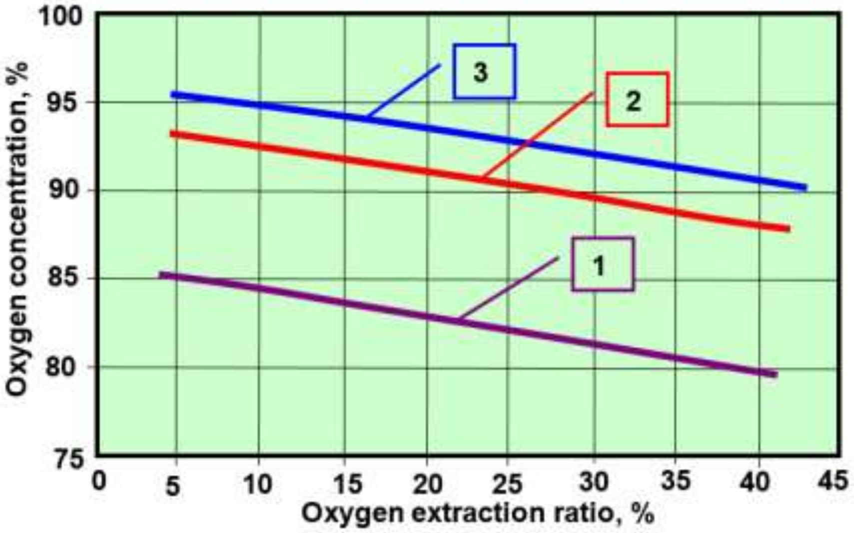

**Fig. 4. Calculated dependences of the concentration of production oxygen on the oxygen extraction ratio from the air during the operation of the PSA unit on zeolites of the 5a, Oxysiv 5 and Oxysiv 7 brands.
1– zeolites CaX; 2 – zeolites Oxysiv 5; 3 – zeolites Oxysiv 7**

Dynamic self-oscillating systems, which are PSA systems, are characterized by complex behavior. While for linear systems it is possible to formulate statements such as if one of the varying parameters increases, the other design parameters will also increase or vice versa. This is not the case with dynamic systems. If you change any parameter in the adsorption phase, it will lead to a change in the parameters in the regeneration phase, and the change in the parameters in the regeneration phase will in turn affect the parameters in the adsorption phase. Therefore, when modeling the operation of PSA units, it is necessary to consider the entire operating process of such a unit as a whole, rather than dividing it into separate phases that can be analyzed separately.

This is fundamentally different from the established practice of engineering calculations and design of technological processes, which is based on decomposition of complex technological schemes and processes into simpler parts that can be analyzed separately.

The Wave approach to the consideration and calculation of PSA plants is ideally suited for these purposes. All phases of plant operation are considered as a whole and the parameters of the plant limit cycles are determined directly as a result of the calculations.

The exclusion of transients from the consideration when using the Wave approach to calculate PSA plants is a major advantage of this method, as it radically simplifies plant calculations.

Conclusions

A prerequisite for the effective operation of the PSA unit is the adsorption of the components of the mixture to be separated at different active centers of the adsorbent surface. An external manifestation of this adsorbent property is the independence of adsorption of one component from the degree of saturation of other components of the mixture.

Even a significant difference in the binding energy of the adsorbed gas molecules with the adsorbent surface, which is externally manifested by the difference in the absolute value of adsorption of gases by a given adsorbent, does not provide effective separation of the gas mixture.

The Wave approach to the analysis and calculation of PSA processes allows finding an analytical solution of the system of differential equations describing the operation of the adsorption apparatus. The analysis of the obtained solution shows that this system of equations in the case of separation of a multicomponent mixture has several solutions.

Conditions have been formulated to ensure the realization of those solutions that provide the most efficient operation of PSA units.

The mathematical model developed on the basis of the wave approach for the analysis and calculation of PSA processes allows to explain the mechanisms that allow to obtain high oxygen concentrations with an extraction ratio of more than 40 % in the best industrial samples of PSA units.

References

[1] U.S. Patent 2,944,627 (1960). Scarstrom, C.W. Metod and apparatus for fractionating mixtures by adsorption.

[2] Shivaji, S. (2002). Pressure Swing Adsorption. *Industrial & Engineering Chemistry Research*, 41(6), 1389–1392. doi:10.1021/ie0109758.

[3] Ruthven, D. M., Farooq, S., Knaebel, K. S. (1994). *Pressure Swing Adsorption*. VCH Publishers Inc. New York.

[4] Ruthven, D. M. (1984). *Principles of Absorption and Absorption Process*, Wiley-InterScience, Hoboken, NY.

[5] Hayashi, S., Kawai, M.; Kaneko, T. (1996). Dynamics of high purity oxygen PSA. *Gas Separation & Purification, 10*(1), 19-23.

[6] Jee, J.-G.; Lee, J.-S.; Lee, C.-H. (2001). Air separation by a small-scale two-bed medical O_2 Pressure Swing Adsorption. *Industrial & Engineering Chemical Research*, (40), 3647–3658.

[7] Ruthven, D. M.; Xu, Z. (1993). Diffusion of Oxygen and Nitrogen in 5A Zeolite Crystals and Commercial 5A Pellets. *Chemical Engineering Science, 48*(18), 3307–3312.

[8] Sherman, J. D. (1999). Synthetic zeolites and other microporous oxide molecular sieves. *Proceedings of the National Academy of Sciences of the United States of America, 96*(7), 3471–3478.

[9] Cruz, P., Santos, J. C., Magalhães, F. D., Mendes, A. (2003). Cyclic adsorption separation processes: Analysis strategy and optimization procedure. *Chemical Engineering Science, 58*(14), 3143–3158.

[10] Santos, J. C., Portugal, A. F., Magalhães, F. D., Mendes, A. (2004). Simulation and optimization of small oxygen pressure swing adsorption units. *Industrial & Engineering Chemistry Research, 43*(26), 8328–8338.

[11] Teague, K. G., Jr., Edgar, T. F. (1999). Predictive dynamic model of a small pressure swing adsorption air separation unit. *Industrial & Engineering Chemical Research, 38*(10), 3761–3775.

[12] Farooq, S.; Ruthven, D. M.; Boniface, H. A. (1989). Numerical-Simulation of a Pressure Swing Adsorption Oxygen Unit. *Chemical Engineering Science, 44*(12), 2809–2816.

[13] Kravchenko, M. B. (2014). [*Wave adsorption. Saarbruecken*], Lap. Lambert Academic Publishing. (in Russian)

[14] Kravchenko, M. B. (2017). Wave mathematical model to describe gas chromatography. *Refrigeration Engineering and Technology, 53*(6), 28–37.

[15] Kravchenko, M. B., Lavrenchenko, G. K. (2019). Effective Use of DP-PSA Gas Separation Technology. *Chemical and Petroleum Engineering, 55*(3-4), 298–305.

[16] Kravchenko, M. B. (2018). Effect of Adsorbent Grain Size on the Pressure Swing Adsorption. *Refrigeration Engineering and Technology*, 54 (1), 24-34.

[17] Mikusiński, J. (1959). *Operational Calculus*. New York: Pergamon Press.

[18] Duhamel, P. (2004). Application of a new finite integral transform method to the wave model of conduction. *International Journal of Heat and Mass Transfer*, 47(3), 573–588.

[19] Cotta, R. M., Knupp, D. C., Naveira-Cotta, C. P., Sphaier, L. A., Quaresma, J. N. N. (2013). Unified Integral Transforms Algorithm for Solving Multidimensional Nonlinear Convection-Diffusion Problems. *Numerical Heat Transfer, Part A: Applications*, 63(11), 840–866.

[20] Queiroz, H., Bentes, F. M., Nóbrega, M. J, Martins, F. B. (2020). A generalized integral transformed technique: literature review and comparative results with finite volume metod. In book: *Atividades Cientificas e Tecnologicas no Campo da Engenharia Mecanica*. Publisher: Atena Editora. Paraná. Brasil.

[21] Santos, J. C. G. F. (2005). *Study of New Adsorbents and Operation Cycles for Medical PSA Units*. Dissertation presented for the degree of Doctor in Chemical Engineering by Universidade do Porto.

[22] Dreisbach, F., Lösch, H. W., Harting, P. (2002). Highest Pressure Adsorption Equilibria Data: Measurement with Magnetic Suspension Balance and Analysis with a New Adsorbent. Adsorbate-volume. *Adsorption, 8*(2), 95-109.

[23] Hutson, N. D., Zajic, S. C., Rege, S. U., Yang, R. T. (2001). *Air Separation by Pressure Swing Adsorption Using Superior Adsorbents*. University of Michigan: Ann Arbor.

[24] Hutson, N. D., Zajic, S. C., Yang, R. T. (2000). Influence of residual water on the adsorption of atmospheric gases in Li-X zeolite: Experiment and simulation. *Industrial &Engineering Chemistry Research, 39*(6), 1775–1780.

[25] D.M. Ruthven; S. Farooq (1990). Air separation by pressure swing adsorption, *Gas Separation & Purification*. 4(3), 141–148.

[26] Chou, C. T.; Huang, W. C. (1994). Incorporation of a Valve Equation into the Simulation of a Pressure Swing Adsorption Process. *Chemical Engineering Science, 49*(1), 75–84.

[27] Feinstein ,V. I., Kobets, Yu. I., Masumov, D. I., Purts, N. A., Shkadov, V. Ya. (2005). [Results of experimental studies of oxygen installations of PSA]. *Industrial gases*, 1, 23–29. (in Russian)

[28] Xu, Mai, Wu, Han-Chun, Lin, Y. S., Deng, Shuguang (2018). Simulation and optimization of pressure swing adsorption process for high-temperature air separation by perovskite sorbents. *Chemical Engineering Journal, 354*, 62–74. doi:10.1016/j.cej.2018.07.080

[29] Kamin, Z., Bahrun, M., Bono, A. (2022). A short review on pressure swing adsorption (PSA) technology for nitrogen generation from air. *AIP Conference Proceedings 2610*, 050006. https://doi.org/10.1063/5.0099702