

МОДЕЛЬ КИНЕТИКИ АДсорбЦИОННОЙ ОЧИСТКИ АТМОСФЕРНОГО ВОЗДУХА ГРАНУЛАМИ ЦЕОЛИТА NaX ПРИ НЕИЗОТЕРМИЧЕСКИХ УСЛОВИЯХ

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На основе обобщенной теории Ленгмюра представлены эквивалентные многокомпонентные изотермы основных примесей атмосферного воздуха (водяной пар, диоксид углерода и ацетилен), с использованием экспериментальных данных их адсорбционной емкости в гранулах цеолита NaX и расчетом константы Генри по температуре кипения при атмосферном давлении, для термодинамических условий в блоке комплексной очистки воздухоразделительной установки ТКДС-100В. Внутригранулярный теплообмен рассмотрен в линейном приближении Глюкауфа с применением суперпозиционного принципа поведения примесей в условиях диффузионного механизма их поглощения (молекулярный, Кнудсеновский, Фольмеровский). Получена модель с сосредоточенными параметрами в виде задачи Коши, причем идентификация кинетических коэффициентов проведена из решения задачи диффузии в шаре при граничных условиях первого рода. Теплоты адсорбций примесей найдены по изостерическому состоянию из двумерного уравнения Ван-дер-Ваальса с использованием соотношения Вант-Гоффа. Нестационарная среднеобъемная температура гранулы вычислена из решения начально-краевой задачи для уравнения теплопроводности шара с граничным условием первого рода на его поверхности, в предположении теплового равновесия фаз, и объемным равномерным тепловым источником, обусловленным теплотой адсорбции. Установлено, что лимитирующим механизмом переноса примесей в гранулах адсорбента является диффузия в микропорах. В условиях пропорциональной зависимости параметра Ленгмюровской изотермы от температуры сделана оценка уменьшения адсорбционной емкости адсорбента с повышением температуры, что позволило с помощью вычислительного эксперимента проанализировать кинетику поглощения основных примесей атмосферного воздуха гранулами цеолита NaX.

Ключевые слова: модель, кинетика, адсорбция, очистка, воздух, цеолит, температура

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MODEL OF KINETICS OF ADSORPTION PURIFICATION OF ATMOSPHERIC AIR BY ZEOLITE NaX GRANULES UNDER NON-ISOTHERMAL CONDITIONS

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Based on the generalized Langmuir theory, equivalent multicomponent isotherms of the main atmospheric air impurities (water vapor, carbon dioxide, and acetylene) are presented, using experimental data on their adsorption capacity in NaX zeolite granules and calculating the Henry constant from the boiling point at atmospheric pressure, for thermodynamic conditions in the block of complex cleaning of the TOPS-100V air separation unit. Intra-granular heat and mass transfer is considered in the linear Gluckauf approximation using the superposition principle of impurities behavior under the conditions of the diffusion mechanism of their absorption (molecular, Knudsenovskiy, Folmerovskiy). A model with lumped parameters is obtained in form of the Cauchy problem, and the identification of the kinetic coefficients is carried out from the solution of the diffusion problem in a ball under boundary conditions of the first kind. The impurities adsorption heats were found from the isosteric state from the two-dimensional equation van-der-Waals using the Van-Hoff ratio. The unsteady average volumetric granule temperature is calculated from the solution of the initial-boundary value problem for the equation of thermal conductivity of a sphere with a boundary condition of the first kind on its surface, under the assumption of thermal equilibrium of the phases, and a volumetric uniform heat source due to the adsorption heat. It was found that the limiting mechanism of impurity transfer in adsorbent granules is diffusion in micropores. Under the conditions of the proportional dependence of the Langmuir isotherm parameter on temperature, an estimate was made of the decrease in the adsorption capacity of the adsorbent with increasing temperature, which made it possible, using a computational experiment, to analyze the kinetics of absorption of the main atmospheric air impurities by granules of NaX zeolite.

Key words: model, kinetics, adsorption, purification, air, zeolite, temperature

INTRODUCTION

Granular synthetic zeolite NaX is the main component of a complex cleaning unit (CCU) of air separation units (ASU) for the oxygen and nitrogen separation from gaseous impurities (vaporous moisture (H₂O), carbon dioxide (CO₂), acetylene (C₂H₂)) of atmospheric air [1]. The exothermicity of the adsorption process reduces the adsorption capacity (static and dynamic) and reduces the efficiency of the adsorbents [2]; therefore, the heat and mass transfer processes accompanying adsorption are of a conjugate nature. In most cases, the presented nonisothermal models are limited to single-species adsorption [3], or the dependence of the governing parameters on temperature is neglected [4].

A common feature of solid-phase adsorbents, including zeolites, is their high specific absorption area due to the developed inner pore surface (for zeolites 200-600 m²/g [5], the average pore diameter is 2-10 Å [6]), therefore, the adsorption process proceeds, according to the classical concepts [7], on the surface of the internal granules voids. This requires the transfer of molecules into the granules by the diffusion absorption mechanism with specific features depending on the pore size [8]. Diffusion in pores and molecular diffusion have the same driving force – the concentration gradient, however, their difference is that diffusion in pores occurs as a result of molecules collisions with walls, and molecular diffusion is initiated by collisions with other molecules in pores, and these two diffusions

types coincide when the pore diameter is large enough [9]. In the limiting case (the pore radius is less than the free path of molecules), pore diffusion becomes Knudsen diffusion [10]:

$$D_k = 9700 \cdot r_p (t/\mu)^{1/2}, \quad (1)$$

where r_p is the average pore radius, cm; t is temperature, K; μ is the molecular weight of the adsorbent, g/mol. To establish the relationship between diffusion in pores D_p and molecular diffusion, a semiempirical relation is used [8]

$$D_p = \varepsilon_p D_M / l_p, \quad (2)$$

where ε_p is the porosity of the adsorbent granules (0.05-0.5); l_p is the pore tortuosity factor (for example, according to [11], it can reach values up to 100, but in most cases for zeolites it lies within 3.3-3.6); to calculate the molecular diffusion coefficient, the Chapman-Enskiy formula is applicable [12]

$$D_M = \frac{0.0018583 \cdot t^{3/2} (1/\mu_A + 1/\mu_B)^{1/2}}{p \sigma_{12}^2 \Omega(\varepsilon/kt)}, \quad (3)$$

where μ_A, μ_B – molecular weights of gases A and B , g/mol; p – pressure, atm; $\sigma_{12} = (\sigma_A + \sigma_B)/2$; σ_A, σ_B – diameters of molecules of gases A and B , Å; $\Omega(\varepsilon/kt)$ is a dimensionless function of temperature and intermolecular potential field for molecules A and B ; ε/k is the Lennard-Johnson potential, K. If diffusion in pores and Knudsen diffusion occur simultaneously, then the joint diffusion coefficient is determined by the Bosanquit relation [12]

$$D_{pk}^{-1} = D_p^{-1} + D_k^{-1}. \quad (4)$$

Folmer diffusion characterizes the mass transfer of already adsorbed molecules over the inner pore surface [13]

$$\lg D_s = 1.8 - 0.20 \Delta Q / (mRt), \quad (5)$$

where ΔQ is the heat of adsorption, J/mol; R – universal gas constant, J/(mol·K); m – surface index.

Due to the fact that the driving force of various diffusion mechanisms directly depends on the adsorbate concentration outside the granules, the heat and mass transfer inside them determines the adsorption process kinetics, it is necessary to consider together with the entire adsorbent layer [14]. In this case, the mixed kinetics of pore and surface mass transfer under the assumption of the diffusion mechanisms and monodisperse granules sphericity summation is described by the equation [8]

$$\varepsilon_p \frac{\partial c(r, \tau)}{\partial \tau} + \rho_p \frac{\partial q(r, \tau)}{\partial \tau} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D_{pk} r^2 \frac{\partial c(r, \tau)}{\partial r} \right] + \frac{\rho_p}{r^2} \left[D_s r^2 \frac{\partial q(r, \tau)}{\partial r} \right], \quad (6)$$

where τ is time, s; r_g – radius of the granule, m; r – current radius ($0 \leq r \leq r_g$), m; $c(r, \tau)$, $q(r, \tau)$ – are the local

concentrations of the adsorbate in the pore medium and the adsorbed phase within the granule, kg/m³, wt. shares; ρ_p is the density of the granule, kg/m³. The dependence of the diffusion coefficients (1)-(5) on temperature requires knowledge of the temperature fields inside the granules associated with the adsorption heat and the conditions at its outer boundary [15] using an equation of the thermal conductivity type, as well as the relationship between $c(r, \tau)$ and $q(r, \tau)$, assuming that they are in equilibrium [16]

$$q = f(c). \quad (7)$$

In addition to this, an appropriate set of initial and boundary conditions is required. If we take into account the adsorbate multicomponent, then it turns out that the problem can be solved only numerically, while there is no certainty about the existence and uniqueness of the result obtained [17]. The implementation of such an approach in a parametric search for the determination of effective modes of adsorbents operation is apparently justified, but when evaluating pre-design solutions for a reasonable choice of separation equipment, when it is necessary to carry out optimization procedures, a more flexible toolkit is needed in the form of models with lumped parameters, which integrally takes into account the adsorption process reference features. This study is devoted to the development of such a model.

MULTICOMPONENT IMPURITY ISOTHERMES

Let gaseous impurities in atmospheric air have the following subscript numbering: H₂O – 1; CO₂ – 2; C₂H₂ – 3. According to the generalized Langmuir theory [18], the equivalent expression for the i -th ($i = \overline{1,3}$) adsorption component has the form

$$q_i = \frac{a_i p_i}{1 + \sum_{j=1}^3 b_j p_j}, \quad (8)$$

where p_i is the partial pressure of the i -th component of the impurity, Pa; a_i, b_i – are parameters determined from adsorption isotherms in a monovariant presence in atmospheric air, Pa⁻¹, that is

$$q_i^0 = \frac{a_i p_i^0}{1 + b_i p_i^0}. \quad (9)$$

The adsorption capacity of impurities in granules of zeolite NaX according to [19] is given in Table 1. For zeolites in [20] it was found that the Henry constant of the i -th adsorbate K_i [mol/(g·Pa)] can be determined by the empirical relation

$$\ln K_i \approx 0.0623 \cdot t_{b_i} - 18.12, \quad (10)$$

where t_{b_i} is the boiling point at atmospheric pressure

of the i -th adsorbate, K ($50 \leq t_{b_i} \leq 350$). It follows from the structure of the Langmuir equation that

$$a_i = b_i q_{m_i} = K_i. \quad (11)$$

Calculations of the values of a_i and b_i (see Table 1) are given for thermodynamic conditions at the entrance to the CCU ASU TOPS-100V [21] ($p_0 = 20$ MPa, $t_0 = 288$ K, density of granules $\rho_p = 1100$ kg/m³ and their diameter $d_g = 4$ mm), while the partial pressures of water vapor, carbon dioxide and acetylene are respectively equal [22]: $p_1^* = 25.8$ kPa; $p_2^* = 0.608$ kPa; $p_3^* = 0.002$ kPa.

Table 1

Isotherms parameters calculation
Таблица 1. Расчет параметров изотерм

Parameter	Adsorbate		
	H ₂ O	CO ₂	C ₂ H ₂
q_{m_i} , kg/m ³	120.0	20.0	60.0
t_{b_i} , K	373.0	194.5	190.0
μ_i , kg/mol	$18.01 \cdot 10^{-3}$	$44.0 \cdot 10^{-3}$	$26.04 \cdot 10^{-3}$
a_i , kg/(m ³ ·Pa)	3308.0	0.069	0.054
b_i , Pa ⁻¹	27.57	$3.45 \cdot 10^{-3}$	$9.05 \cdot 10^{-4}$

From a comparative analysis of isotherms (Fig. 1) it follows that at the beginning the granules are saturated with water vapor, and then with carbon dioxide and acetylene (the same qualitative conclusion was made based on the results of pilot experiments in [19]).

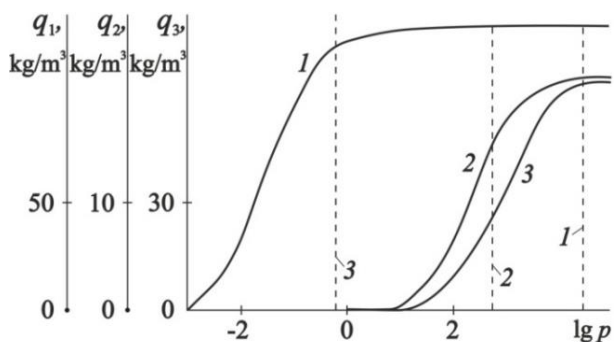


Fig. 1. Isotherms of impurities: 1 – H₂O; 2 – CO₂; 3 – C₂H₂ (the dotted line is the partial pressure of impurities)
Рис. 1. Изотермы примесей: 1 – H₂O; 2 – CO₂; 3 – C₂H₂ (пунктирная линия – парциальные давления примесей)

INTRAGRANULAR MASS EXCHANGE

Regardless of which diffusion mechanism dominates during the transport of adsorbates into a granule, quantitative analysis requires the joint solution of equations (6) and (7) for each adsorbate with additional conditions. This problem is simplified using

the postulate of Gluckauf [23] that the rate of absorption of adsorbates by a granule is linearly proportional to the driving force of the process, which is defined as the difference between the concentration on the surface of the granule q_{m_i} and the superposition of the average

$$\begin{cases} \frac{d\bar{q}_i(\tau)}{d\tau} = k_{p_i} [q_{m_i} - \bar{q}_i(\tau)], \quad i = \overline{1,3} \\ \frac{d\bar{q}(\tau)}{d\tau} = \sum_{i=1}^3 \frac{d\bar{q}_i(\tau)}{d\tau} \end{cases} \quad (12)$$

with initial conditions

$$\bar{q}_i(0) = \bar{q}_i^0 = \text{const} \quad (13)$$

and limitation on adsorption capacity

$$\bar{q}(\tau_0) = \bar{q}^0 = \text{const}, \quad (14)$$

where \bar{q}_i is the current concentration of the i -th adsorbate in the adsorbent, kg/m³; \bar{q} – total concentration of adsorbates in the adsorbent granule, kg/m³; k_{p_i} – kinetic coefficients, s⁻¹, which are related to the geometrical dimensions of the granule, its physical characteristics and the diffusion mechanism; τ_0 – time to reach 99% of the adsorption capacity of the granule, s. The identification k_{p_i} was carried out for the quasi-isosteric adsorption mode (practically unchanged temperature and pressure). If, as in [8], we assume that in (6) $(\epsilon_p / \rho_p) \partial c_i(r, \tau) / \partial \tau \ll \partial q_i(r, \tau) / \partial \tau$ and f in (7) is differentiable with respect to c_i (the Langmuir relation assumes this for $c_i \in [0, \infty)$, which is explicitly related to p_i through the equation of state for an ideal gas), that is $dq_i = f(c_i)dc_i$, then from (6) it follows

$$\frac{\partial q_i(r, \tau)}{\partial \tau} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{e_i} r^2 \frac{\partial q_i}{\partial r} \right), \quad (15)$$

where the effective diffusion coefficient is

$$D_{e_i} = \frac{D_{p k_i}}{f'(c_i) \rho_p} + D_{s_i} = \text{const} \quad (16)$$

Equation (15) is supplemented with the initial condition

$$q_i(r, 0) = 0, \quad (17)$$

the condition for the concentration constancy of the i -th adsorption phase at the outer boundary of the granule

$$q_i(r_g, \tau) = q_{m_i} \quad (18)$$

and the axisymmetry condition

$$\frac{\partial q_i(0, \tau)}{\partial r} = 0. \quad (19)$$

Solution of the initial-boundary value problem (15), (17) - (19) [24]

$$q_i(r, \tau) = q_{m_i} + \frac{2r_g q_{m_i}}{\pi r^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \sin\left(\frac{n\pi r}{r_g}\right) \exp\left(-\frac{D_{e_i} n^2 \pi^2 \tau}{r_g^2}\right). \quad (20)$$

It follows from (20) that

$$\bar{q}_i(\tau) = q_{m_i} + \frac{6q_{m_i}}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_{e_i} n^2 \pi^2 \tau}{r_g^2}\right), \quad (21)$$

$$\frac{d\bar{q}_i(\tau)}{d\tau} = \frac{6q_{m_i} D_{e_i}}{r_g^2} \sum_{n=1}^{\infty} \exp\left(-\frac{D_{e_i} n^2 \pi^2 \tau}{r_g^2}\right). \quad (22)$$

Substituting (21) and (22) into system (12), and bearing in mind that for $D_{e_i} n^2 \pi^2 \tau / r_g^2 \gg 1$

$$\sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_{e_i} n^2 \pi^2 \tau}{r_g^2}\right) \Big/ \sum_{n=1}^{\infty} \exp\left(-\frac{D_{e_i} n^2 \pi^2 \tau}{r_g^2}\right) \rightarrow 1,$$

we get

$$K_{p_i} = \pi^2 D_{e_i} / r_g^2. \quad (23)$$

IMPURITIES ADSORPTION HEAT

The isosteric adsorption heat of the i -th adsorbate was determined from the theoretical adsorption isotherm based on the two-dimensional Van-der-Waals equation [25]

$$p_i = \xi R_i \bar{t} \frac{q_i}{q_{m_i} - q_i} \exp\left(\frac{q_i}{q_{m_i} - q_i} - \frac{2a_{cr_i} q_i}{b_{cr_i} R_i \bar{t} q_{m_i}}\right), \quad (24)$$

where R_i is the gas constant of the i -th adsorbate, J/(kg·K); \bar{t} – average volumetric granule temperature, K; ξ – thermodynamic constant, Pa·kg/J; a_{cr_i} , b_{cr_i} are critical parameters equal to

$$a_{cr_i} = \frac{27}{8} \frac{R_i}{\mu_i} t_{cr_i} b_{cr_i}, \quad b_{cr_i} = \frac{R_i}{8\mu_i} \frac{t_{cr_i}}{p_{cr_i}}, \quad (25)$$

where t_{cr_i} , p_{cr_i} are the critical temperature and pressure of the i -th adsorbate, respectively K and Pa. According to the van-Hoff equation [12]

$$Q_{st_i} = R_i \bar{t}^2 d \ln p_i / d \bar{t},$$

whence the value of the heat of adsorption follows (Table 2) at $q_i / q_{m_i} \rightarrow 1$

$$\Delta Q_i = Q_{st_i} - R_i \bar{t} = 2 \frac{a_{cr_i}}{b_{cr_i}}. \quad (26)$$

The local temperature of the adsorbate granule porous matrix, under the assumption of phases thermal equilibrium, is determined from the thermal conductivity of a sphere with a uniform volumetric heat source due to the heat of adsorption

$$c_p \rho_p \frac{\partial t(r, \tau)}{\partial \tau} = \frac{\lambda_p}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial t(r, \tau)}{\partial r} \right] + \frac{\Delta Q^* \rho_p}{\varepsilon_p \tau_0}, \quad (27)$$

where λ_p , c_p – thermal conductivity and heat capacity of the adsorbent matrix, respectively, W/(m·K) and J/(kg·K); ΔQ^* – specific heat of adsorption per granule, J/kg,

Table 2

The adsorbates adsorption heat
Таблица 2. Теплоты адсорбции адсорбатов

Parameter	Adsorbate		
	H ₂ O	CO ₂	C ₂ H ₂
R_i , J/(kgK)	461	189	320
t_{cr_i} , K	647.3	304.1	309.0
p_{cr_i} , Pa	214.0·10 ⁵	71.5·10 ⁵	60.9·10 ⁵
a_{cr_i}	1755.4	194.95	677.1
b_{cr_i}	1.743·10 ⁻³	1.005·10 ⁻³	2.029·10 ⁻³
ΔQ , J/mol	36272	17072	17368
ΔQ , J/kg	2.014·10 ⁶	0.388·10 ⁶	0.667·10 ⁶

$$t(r, 0) = t(r_g, \tau) = t_0, \quad \partial t(0, \tau) / \partial r = 0. \quad (28)$$

Solution of the initial-boundary value problem (27) and (28) [26]

$$T(R, \theta) = W \left[\frac{1}{6} (1 - R^2) + \frac{2}{\pi^3 R} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^3} \sin(\pi n R) \exp(-n^2 \pi^2 \theta) \right],$$

where $T(R, \theta) = t(r, \tau) - t_0$; $\theta = \tau a_q / r_g^2$; $a_q = \lambda_p / (\rho_p c_p)$; $R = r / r_g$; $W = \Delta Q^* \rho_p r_g^2 / (\tau_0 \varepsilon_p \lambda_p)$. Average pellet temperature

$$\bar{T}(\theta) = 6W \left[\frac{1}{15} + \frac{1}{\pi^4} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^4} \cos(\pi n) \exp(-n^2 \pi^2 \theta) \right]. \quad (29)$$

COMPUTATIONAL EXPERIMENT

Evaluation of kinetic coefficients k_{p_i} assumes knowledge of the limiting diffusion mechanism in the granule and the corresponding value of the diffusion coefficient, and a comparative analysis using relation (16) (Table 3) shows that $D_{e_i} \approx D_{pk_i}$.

Table 3

Diffusion coefficients and kinetic parameters for
 $t_0 = 288$ K and $p_0 = 20$ MPa

Таблица 3. Коэффициенты диффузии и кинетические параметры для $t_0 = 288$ K и $p_0 = 20$ МПа

Parameter	Adsorbate		
	H ₂ O	CO ₂	C ₂ H ₂
D_{pk_i} , m ² /s	9.653·10 ⁻⁸	5.760·10 ⁻⁸	7.010·10 ⁻⁸
k_{p_i} , s ⁻¹	0.238	0.142	0.173

The time τ_0 of filling the adsorbate granules with adsorbates was calculated as follows. It follows from (12) and (13) that

$$\frac{d\bar{q}_i(\tau)}{d\tau} = k_{p_i} (q_{m_i} - \bar{q}_i^0) \exp(-k_{p_i} \tau) \quad (30)$$

Substitution of (30) into the second equation of system (12) and subsequent integration from 0 to τ_0 ,

taking into account (14), allows obtaining an expression for the total concentration of adsorbates in a granule

$$\bar{q}(\tau_0) = \int_0^{\tau_0} \frac{d\bar{q}(\tau)}{d\tau} d\tau = \sum_{i=1}^3 (q_{m_i} - \bar{q}_i^0) \exp(-k_{p_i} \tau) \quad (31)$$

In view of the fact that $\bar{q}(\tau_0) = 0.99q_{m_i}$, from (31), $\tau_0 = 4.4$ s was calculated. Since $c_p = 870$ J/(kg·K), $\lambda_p = 0.14$ W/(m·K) [14], therefore $\theta_0 = \tau_0 a_q / r_g^2 = 0.16$ and, according to (29), the increase in the temperature of the adsorbent granule due to adsorption absorption will be ≈ 4 K. If in (11) we restrict ourselves to the linear approximation of the parameter of the Langmuir isotherm on the temperature $b_i \sim t$, then $q_{m_i} = \alpha_i K_i / t$ the coefficients α_i for the thermodynamic conditions at the entrance to the adsorber are calculated (Table 4).

Table 4

The adsorption capacity of zeolite for impurities at $t = 292$ K

Таблица 4. Адсорбционная емкость цеолита по примесям при $t = 292$ K

Parameter	Adsorbate		
	H ₂ O	CO ₂	C ₂ H ₂
α_i	10.447	$83.48 \cdot 10^3$	$32.0 \cdot 10^4$
q_{m_i}	118.35	19.72	59.38

Integration results (12) with initial conditions (13), when $\bar{q}_i^0 = 0$

$$\bar{q}_i(\tau) = q_{m_i} [1 - \exp(-k_{p_i} \tau)] \quad (32)$$

$$\bar{q}(\tau) = \sum_{i=1}^3 q_{m_i} [1 - \exp(-k_{p_i} \tau)] \quad (33)$$

Calculations using relations (32) and (33) in the presence of a restrictive condition on the adsorption capacity (14) show (Fig. 2) that the influence of the ad-

sorption heat during the purification of atmospheric air cannot be neglected, since this can lead to the appearance of a "breakthrough" concentration impurities before the development of the CCU. For example, in this case, with a six-hour adsorption cycle, a decrease in the adsorption capacity by $\approx 1\%$ due to an increase in the temperature of the adsorbent granule by 4 K reduces the operating time by 0.5 h.

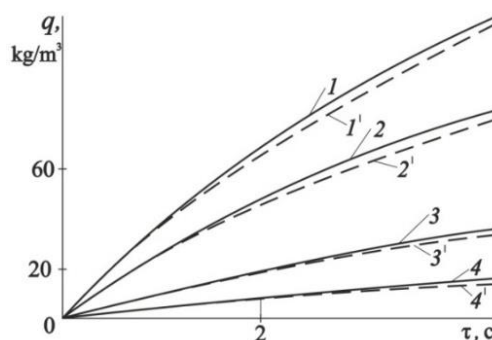


Fig. 2. Kinetics of intragranular adsorption of impurities at 288 K (solid curves) and 292 K (dotted curves): 1, 1' – the total concentration of impurities; 2, 2' – water vapor; 3, 3' – acetylene; 4, 4' – carbon dioxide

Рис. 2. Кинетика внутригранулярной адсорбции примесей при 288 K (сплошные кривые) и 292 K (пунктирные кривые): 1, 1' – суммарная концентрация примесей; 2, 2' – водяной пар; 3, 3' – ацетилен; 4, 4' – диоксид углерода

CONCLUSION

The presented tools for assessing the adsorption heat effect on the intragranular kinetics of adsorption absorption of the main gaseous impurities from the atmospheric air by the NaX zeolite makes it possible to evaluate the purification efficiency.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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ЛИТЕРАТУРА

- Kohla L., Nielsen R. Gas purification. Houston: Gulf Professional Publ. 1997. 900 p.
- Ray S., Das G. Process equipment and plant design. NY: Elsevier. 2020. 882 p.
- Murathatunyaluk S., Srichanvichit K., Anantpinijwatna A., Kitchaiya P. Modeling of non-isothermal adsorption process in a silica gel desiccant packed bed. In: 28th European symposium on computer aided process engineering. Graz (Austria): Elsevier. 2018. P. 49–54. DOI: 10.1016/B978-0-444-64235-6.50011-5.
- Montastruc L., Floquet P., Mayer V., Nikov I., Domenech S. Isothermal or non isothermal modeling in a pellet adsorbent: application to adsorption heat pumps. *Comp. Aid. Chem. Eng.* 2009. V. 27. P. 465–470. DOI: 10.1016/S1570-7946(09)70298-6.
- Seader J.D., Henley J.E., Roper D.K. Separation process principles. Hobokon, NJ, USA: John Wiley & Sons. 2011. 821 p.

REFERENCES

- Kohla L., Nielsen R. Gas purification. Houston: Gulf Professional Publ. 1997. 900 p.
- Ray S., Das G. Process equipment and plant design. NY: Elsevier. 2020. 882 p.
- Murathatunyaluk S., Srichanvichit K., Anantpinijwatna A., Kitchaiya P. Modeling of non-isothermal adsorption process in a silica gel desiccant packed bed. In: 28th European symposium on computer aided process engineering. Graz (Austria): Elsevier. 2018. P. 49–54. DOI: 10.1016/B978-0-444-64235-6.50011-5.
- Montastruc L., Floquet P., Mayer V., Nikov I., Domenech S. Isothermal or non isothermal modeling in a pellet adsorbent: application to adsorption heat pumps. *Comp. Aid. Chem. Eng.* 2009. V. 27. P. 465–470. DOI: 10.1016/S1570-7946(09)70298-6.
- Seader J.D., Henley J.E., Roper D.K. Separation process principles. Hobokon, NJ, USA: John Wiley & Sons. 2011. 821 p.

6. **Wankat P.C.** Separation processes engineering: Includes mass transfer analysis. NY: Prentice Hall. 2012. 955 p.
7. **Толмачев А.М.** Адсорбция газов, паров и растворов. М.: Изд. группа «Граница». 2012. 241 с.
8. **Tien C.** Adsorption calculations and modelling. Boston, USA: Butterworth-Heinemann. 1994. 244 p. DOI: 10.1016/B978-0-7506-9121-5.50013-6.
9. **Gautam R.K., Chattopadhyaya M.C.** Nanomaterials for wastewater remediation. NY: Butterworth-Heinemann. 2016. 366 p. DOI: 10.1201/9781315368108.
10. **Li S., Xin F., Li L.** Reaction NY: Butterworth-Heinemann. 2017. 676 p.
11. **Zhao J.C.** Methods for phase diagram determination. NY: Elsevier. Science. 2007. 520 p.
12. **Suzuki M.** Adsorption engineering. Tokyo: Kodansha Ltd. 1990. 278 p.
13. **Cheng D., Peters E., Knipers J.** Numerical modeling of flow and coupled mass and heat transfer in an adsorption process. *Chem. Eng. Sci.* 2016. V. 152. P. 413–425. DOI: 10.1016/j.ces.2016.06.036.
14. **Karge H.G., Weitkamp J.** Molecular sieves. Science and Technology. Adsorption and diffusion. V. 7. Berlin: Springer-Verlag Berlin Heidelberg. 2008. 400 p. DOI: 10.1007/978-3-540-73966-1.
15. **Danilov V.A., Schepper P., Cousin-Saint-Remi J., Denayer J.F.M.** Concentration and temperature profiles in a fixed bed column based on an analytical solution of the axial dispersion model for binary and multicomponent non-isothermal adsorption process. *Comp.Chem. Eng.* 2019. V. 123. P. 76–86. DOI: 10.1016/j.compchemeng.2018.12.026.
16. **Ruthven D.M.** Principles of adsorption and adsorption processes. NY: Wiley. 1984. 464 p.
17. **Solmus I., Rees D.A.S., Yamali C., Baker D., Kaftanoglu B.** Numerical investigation of coupled head and mass transfer inside the adsorbent bed of an adsorption cooling unit. *J. Refrigeration.* 2012. V. 35. P. 652–662. DOI: 10.1016/j.jrefrig.2011.12.006.
18. **Wang J., Guo X.** Adsorption isotherm models: Classification, physical meaning, application and solving method. *Chemosphere.* 2020. V. 258. Art. 127279. DOI: 10.1016/j.chemosphere.2020.127279.
19. **Денисенко Г.Ф., Файнштейн В.И.** Техника безопасности при производстве кислорода. М.: Metallurgiya. 1968. 220 с.
20. **Tien C.** Introduction to adsorption. Basics, Analysis and Application. Amsterdam: Elsevier Inc. 2019. 205 p.
21. **Филимонова О.Н., Викулин А.С., Енютина М.В., Иванов А.В.** Влияние входной температуры на изотермическую очистку газа от монопримеси неподвижным слоем адсорбента. *Изв. вузов. Химия и хим. технология.* 2020. Т. 63. Вып. 9. С. 88–92.
22. **Варгафтик Н.Б.** Справочник по теплофизическим свойствам газов и жидкостей. М.: Наука, 1972. 721 с.
23. **Glueckauf E., Coates J.I.** Theory of chromatography. Part IV. The influence of incomplete equilibrium on the front boundary of chromatograms and on the effectiveness of separation. *J. Chem. Soc.* 1947. P. 1315–1321. DOI: 10.1039/jr9470001315.
24. **Largitte L., Pasquier R.** A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chem. Eng. Res. Desing.* 2016. V. 109. P. 495–504. DOI: 10.1016/j.cherd.2016.02.006.
25. **Myers A.L., Prousnitz J.M.** Prediction of the adsorption isotherm by principle of corresponding states. *Chem. Eng. Sci.* 1965. V. 20. P. 549–556. DOI: 10.1016/0009-2509(65)80022-7.
26. **Карслоу Г., Егер Д.** Теплопроводность твердых тел. М.: Наука. 1964. 488 с.
6. **Wankat P.C.** Separation processes engineering: Includes mass transfer analysis. NY: Prentice Hall. 2012. 955 p.
7. **Tolmachev A.M.** Adsorption of gases, vapors and solutions. M.: Izd. gruppa «Granitsa». 2012. 241 p. (in Russian).
8. **Tien C.** Adsorption calculations and modelling. Boston, USA: Butterworth-Heinemann. 1994. 244 p. DOI: 10.1016/B978-0-7506-9121-5.50013-6.
9. **Gautam R.K., Chattopadhyaya M.C.** Nanomaterials for wastewater remediation. NY: Butterworth-Heinemann. 2016. 366 p. DOI: 10.1201/9781315368108.
10. **Li S., Xin F., Li L.** Reaction NY: Butterworth-Heinemann. 2017. 676 p.
11. **Zhao J.C.** Methods for phase diagram determination. NY: Elsevier. Science. 2007. 520 p.
12. **Suzuki M.** Adsorption engineering. Tokyo: Kodansha Ltd. 1990. 278 p.
13. **Cheng D., Peters E., Knipers J.** Numerical modeling of flow and coupled mass and heat transfer in an adsorption process. *Chem. Eng. Sci.* 2016. V. 152. P. 413–425. DOI: 10.1016/j.ces.2016.06.036.
14. **Karge H.G., Weitkamp J.** Molecular sieves. Science and Technology. Adsorption and diffusion. V. 7. Berlin: Springer-Verlag Berlin Heidelberg. 2008. 400 p. DOI: 10.1007/978-3-540-73966-1.
15. **Danilov V.A., Schepper P., Cousin-Saint-Remi J., Denayer J.F.M.** Concentration and temperature profiles in a fixed bed column based on an analytical solution of the axial dispersion model for binary and multicomponent non-isothermal adsorption process. *Comp.Chem. Eng.* 2019. V. 123. P. 76–86. DOI: 10.1016/j.compchemeng.2018.12.026.
16. **Ruthven D.M.** Principles of adsorption and adsorption processes. NY: Wiley. 1984. 464 p.
17. **Solmus I., Rees D.A.S., Yamali C., Baker D., Kaftanoglu B.** Numerical investigation of coupled head and mass transfer inside the adsorbent bed of an adsorption cooling unit. *J. Refrigeration.* 2012. V. 35. P. 652–662. DOI: 10.1016/j.jrefrig.2011.12.006.
18. **Wang J., Guo X.** Adsorption isotherm models: Classification, physical meaning, application and solving method. *Chemosphere.* 2020. V. 258. Art. 127279. DOI: 10.1016/j.chemosphere.2020.127279.
19. **Denisenko G.F., Fainshtein V.I.** Oxygen production safety. M.: Metallurgiya. 1968. 220 p. (in Russian).
20. **Tien C.** Introduction to adsorption. Basics, Analysis and Application. Amsterdam: Elsevier Inc. 2019. 205 p.
21. **Filimonova O.N., Vikulin A.S., Enyutina M.V., Ivanov A.V.** Inlet temperature influence on isothermal gas cleaning from mono-impurities by fixed layer of adsorbent. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2020. V. 63. N 9. P. 88–92. DOI: 10.6060/ivkkt.20206309.6247.
22. **Vargaftik N.B.** Handbook of thermophysical properties of gases and liquids. M.: Nauka. 1972. 721 p. (in Russian).
23. **Glueckauf E., Coates J.I.** Theory of chromatography. Part IV. The influence of incomplete equilibrium on the front boundary of chromatograms and on the effectiveness of separation. *J. Chem. Soc.* 1947. P. 1315–1321. DOI: 10.1039/jr9470001315.
24. **Largitte L., Pasquier R.** A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chem. Eng. Res. Desing.* 2016. V. 109. P. 495–504. DOI: 10.1016/j.cherd.2016.02.006.
25. **Myers A.L., Prousnitz J.M.** Prediction of the adsorption isotherm by principle of corresponding states. *Chem. Eng. Sci.* 1965. V. 20. P. 549–556. DOI: 10.1016/0009-2509(65)80022-7.
26. **Carlslaw H.S., Jaeger J.C.** Conduction of heat in solids. Oxford: Oxford University Press, USA. 1959. 510 p.

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