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КОРОТКОЦИКЛОВАЯ БЕЗНАГРЕВНАЯ АДСОРБЦИЯ ДЛЯ ИЗВЛЕЧЕНИЯ ВОДОРОДА, КИСЛОРОДА И АЗОТА ИЗ ГАЗОВЫХ СМЕСЕЙ: МАТЕМАТИЧЕСКОЕ МОДЕЛИРОВАНИЕ, ОПТИМИЗАЦИЯ РЕЖИМОВ ФУНКЦИОНИРОВАНИЯ И ПРОЕКТИРОВАНИЕ УСТАНОВОК

Е.И. Акулинин, О.О. Голубятников, С.И. Дворецкий

Анализ и обобщение мирового опыта в области решения задач математического моделирования, оптимизации режимов функционирования и проектирования технологических процессов разделения газовых смесей и извлечения ценных газов по способу короткоцикловой безнагревной адсорбции позволили вскрыть противоречия и сформулировать ряд проблем, связанных с дальнейшим развитием и интенсификацией циклических адсорбционных процессов, совершенствованием их аппаратурно-технологического оформления, методологии создания и исследования установок короткоцикловой безнагревной адсорбции. В настоящее время разработаны: 1) метод математического моделирования динамики технологического процесса разделения газовых смесей и извлечения продуктовых газов (водорода, кислорода, азота и др.), отличающийся учетом влияния процессов массо- и теплопереноса в газовой и твердой фазах на кинетику диффузионного переноса адсорбтива (водорода, диоксида и оксида углерода, кислорода, азота) в пределах единичного адсорбера, возмущающих воздействий (состава, температуры и давления исходной газовой смеси (синтез-газа, атмосферного воздуха) и увязкой между собой моделей всех аппаратов и устройств, входящих в состав установки короткоцикловой безнагревной адсорбции; 2) процедура построения математической модели процесса разделения многокомпонентной газовой смеси и извлечения продуктового газа с использованием формулы аналитического метода, состоящей из следующих пяти этапов: получение структуры математической модели; получение экспериментальных данных об исследуемомом технологическом процессе/объекте в лабораторных условиях; определение вектора параметров приближенной математической модели; анализ адекватности построенной математической модели; обеспечение адекватности математической модели; 3) методы решения уравнений математической модели процесса короткоцикловой безнагревной адсорбции, позволяющие получать устойчивые конечно-разностные схемы и исключать возникновение возмущений (осцилляций) из-за наличия «крутых» адсорбционных фронтов и нелинейности модели; 4) подходы к решению задач оптимизации режимов функционироания и проектирования установок короткоцикловой безнагревной адсорбции: Blackbox Optimization и Simultaneous Tailored Optimization, сочетающие высокоэффективные методы оптимизации (последовательного квадратичного программирования, ветвей и границ и др.) и солверы пакетов прикладных программ MatLab и gPROMS. В статье проводится анализ и систематизация построения моделей и методов математического моделирования циклических адсорбционных процессов, постановок задач оптимизации режимов и проектирования для извлечения водорода, кислорода и азота из газовых смесей; математического, алгоритмического и информационного обеспечения для проектирования экономичных "конструкций" циклических установок адсорбционного разделения многокомпонентных газовых смесей. Дается сравнительная оценка эффективности и целесообразности предлагаемых подходов и методов к их решению, оценивается перспективность направлений дальнейшего развития процессов разделения и очистки газовых смесей по способу короткоцикловой безнагревной адсорбции с использованием современных средств и методов процессов и аппаратов химической технологии, системного анализа, математического моделирования и теории опти-

мизации (гибкости), которые наряду с интенсивно развивающимися средствами вычислительной техники позволяют создавать работоспособные энерго- и ресурсосберегающие химико-технологические процессы и установки в условиях неопределенности исходных данных.

Ключевые слова: короткоцикловая безнагревная адсорбция, водород, кислород, азот, адсорбент, изотерма, режим стационарного периодического процесса, математическое моделирование, оптимизация, проектирование, неопределенности, численные методы

PRESSURE SWING ADSORPTION FOR RECOVERY HYDROGEN, OXYGEN AND NITROGEN FROM GAS MIXTURES: MATHEMATICAL MODELING, OPTIMIZATION AND UNITS DESIGN

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The analysis and generalization of foreign and domestic experience in solving problems of mathematical modeling, regime optimization and design of technological processes for separating gas mixtures and extracting valuable gases by the method of pressure swing adsorption made it possible to reveal contradictions and formulate a number of problems associated with the further development and intensification of cyclic adsorption processes, improvement of their equipment and technological design, as well as methodology for creating and studying pressure swing adsorption units. Currently, the following methods and approaches have been developed: 1) a mathematical modeling method for the dynamics of the technological process for separating gas mixtures and extracting product gases (hydrogen, oxygen, nitrogen, etc.), where the effect of mass and heat transfer processes in the gas and solid phases on the kinetics of diffusion transfer of the adsorptive (hydrogen, carbon dioxide and monoxide, oxygen, nitrogen) within a single adsorber, disturbing influences (composition, temperature and pressure of the initial gas mixture (synthesis gas, atmospheric air) and the interconnection of models of all apparatuses and devices involved in pressure swing adsorption are considered; 2) a procedure for constructing a mathematical model for the process of multicomponent gas mixture separation and product gas extraction using the analytical method formula, which consists of the following five steps: obtaining the structure of the mathematical model; obtaining experimental data on the investigated technological process / object in laboratory conditions; determining the vector of parameters in the approximate mathematical model; analyzing the adequacy of the constructed mathematical model; ensuring the adequacy of the mathematical model; 3) methods for solving the mathematical model equations of the pressure swing adsorption process, which allow obtaining stable finite-difference schemes and excluding the occurrence of disturbances (oscillations) due to the presence of "steep" adsorption fronts and nonlinearity of the model; 4) approaches to solving the optemization problems of the operation and design regimes in pressure swing adsorption units: Blackbox Optimization and Simultaneous Tailored Optimization combining highly efficient optimization methods (sequential quadratic programming, branches and boundaries, etc.) and solvers of the MatLab and gPROMS software packages. The article analyzes and systematizes the process of constructing models and methods of mathematical modeling for cyclic adsorption processes, formulations of regime optimization and design problems for hydrogen, oxygen and nitrogen extraction from gas mixtures. Mathematical, algorithmic and information support for designing economical "structures" of pressure swing adsorption units for separating multicomponent gas mixtures is considered. A comparative assessment of the effectiveness and feasibility of the proposed approaches and methods is given. The paper evaluates the prospects for the further development of gas mixture separation and purification processes by the method of pressure swing adsorption using modern means and methods of chemical engineering processes and devices, system analysis, mathematical modeling and optimization (flexibility) theory, which, along with the intensively developing computer technology, make it possible to create efficient energy and resource-saving chemical engineering processes and units under conditions of uncertainty in the source data.

Key words: pressure swing adsorption, hydrogen, oxygen, nitrogen, adsorbent, isotherm, cyclic steady state, mathematical modeling, optimization, design, uncertainties, numerical methods

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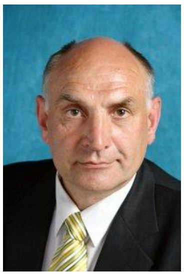

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INTRODUCTION

The annual growth in the production of high-purity gases in the world market over the past decade is ~ 5-7%, and the total production of gases such as hydrogen, oxygen and nitrogen is estimated at about 2/3 of the world industrial production of all industrial gases [1-3]. Hydrogen, oxygen and nitrogen are widely used in various industries and the social sphere, in particular, in ferrous metallurgy, aluminum production, chemical and food industries, medicine, life support systems, fish farming, etc. [1-3]. According to statistics, the total consumption of hydrogen, oxygen and nitrogen doubles every 15 years [1-3].

The most widespread and effective method for separating gas mixtures on solid adsorbents is the pressure swing adsorption method (PSA) proposed in the USA in 1958 by Charles W. Ckarstrom. This method does not involve an external heat source, and the adsorption step is carried out at a higher pressure than the desorption step [4].

The Ckarstrom method has become widespread in chemical engineering for solving tasks of practical importance: in preparation of natural and associated petroleum gas, hydrogen extraction and concentration in the oil refinery cycles, separation of hydrogen from nitrogen, methane and argon in streams of ammonia purge gas [2]; air oxygen enrichment for medical purposes [1]; development of air purification and regeneration systems for habitable objects and oxygen-producing units of pilot life support systems [1]. Nitrogen is widely used in the chemical industry (hardening, carburizing, brazing, annealing, sintering of metals) to create an atmosphere for long-term storage of food products and agricultural fruit and vegetable products, as well as to ensure explosion and fire safety conditions in industrial premises [5].

Hydrogen is extracted from gases of conversion and oxidation of hydrocarbons, refinery gases, synthesis gas, etc. containing such components as CO_2, CO, N_2, CH_4, H_2O, H_2S (and other impurities, the concentration of which does not exceed 0.01 vol.%) in various combinations; oxygen and nitrogen are extracted from atmospheric air. PSA units allow to extract hydrogen with a purity of up to 99.99 vol. %, with a capacity of up to 50,000 nm^3/h and a cost price of ~ 2.5-5 $ per 1 kg of hydrogen [2]; oxygen with a purity of up to 95.5 vol.% and higher, a capacity of up to 6000 nm^3/h and energy consumption of ~ 200-600 kW·h/t [1]; nitrogen with a purity of up to 99.9995 vol.% and a capacity of up to 10000 nm^3/h [5].

The technological scheme for gas mixture separation according to the PSA method consists of a system of adsorbers (from 2 or more) filled with a corresponding adsorbent, a compressor and supplementary equipment (a pressure tank, a receiver, a system of filters, sensors and valves controlled by a microprocessor). The principle of the unit operation is as follows. The initial gas mixture, preliminarily purified from suspensions, is compressed to a predetermined operating pressure in the compressor and then enters the inlet of the first adsorber (adsorption step) in the form of a feed stream with a known concentration of the extracted gas; the pressure tank smoothes out the pressure pulsations at the compressor outlet. The product flow enriched with the extracted component leaves the first adsorber at the outlet pressure and enters the product collector (receiver); the difference between the outlet pressure and the inlet pressure is due to the pressure loss during the gas mixture filtration through the adsorbent bed.

A possible sequence of steps (regimes) in the technological scheme for the implementation of the gas mixture separation process by the PSA method includes the following steps (regimes): adsorption, pressure relief, adsorbent regeneration, and pressure increase. During a process cycle, one of the adsorbers is in the adsorption regime, while another one is in the adsorbent regeneration regime. After the adsorbent saturation, a sign of which is a sharp decrease in the concentration of the released component in the outlet product flow down to the concentration in the inlet flow, the first adsorber switches to the adsorbent regeneration regime. The adsorbers work in antiphase: when one of them is in the adsorption regime, the other at this time is in the adsorbent regeneration regime. Part of the product flow is used in the regeneration regime in sequence to purge the adsorber and to fill it. In multi-adsorber schemes, in order to increase the degree of target gas extraction and reduce energy costs for compressor equipment, it is also possible to use pressure equalization steps between adsorbers.

PSA units differ in the way they create driving force and operate from a source of excess pressure (and/or vacuum). In vacuum pressure swing adsorption units (VPSA), the pressure is above atmospheric at the adsorption step and below atmospheric by about 0.5 atm at the desorption step [6-9]. In vacuum swing adsorption (VSA) units, the pressure at the adsorption step is equal to atmospheric, and at the desorption step it is ~ 0.15-0.3 atm [10-12]. PSA processes are also clssified into three groups according to the duration of the full cycle: in traditional PSA processes, the cycle duration is more than 1 min [1]; in rapid PSA processes (RPSA) – from 0.1 to 1 min [9, 13-15], in ultra-rapid PSA processes (ultra RPSA) – less than 0.1 min [16, 17].

Microporous adsorbents which have high selectivity to the accompanying non-target components of the gas mixture are used as adsorbents for extracting hydrogen, oxygen and nitrogen from gas mixtures. In particular, both industrial zeolites NaX (13X) [13, 18, 19], CaA (5A) [11, 14, 15, 18, 20-22], LiLSX (LiX) [6, 9, 11, 16, 18, 23] and promising silver-containing zeolites AgLiLSX [8, 22, 24], Ag-ETS-10 [25, 26], as well as perovskites [27], possessing high selectivity to argon and making it possible to obtain oxygen at the outlet with a purity up to 99.5 vol. %, are used to extract oxygen and nitrogen from the air. To extract hydrogen from synthesis gases, various brands of activated carbons [28-31], metal-organic framework structures MOF (CuBTC, Cu-TDPAT) [32, 33], industrial zeolites CaA (5A) [5, 34-36], and NaX (13X) [37, 38], which have high selectivity to the synthesis gas components accompanying hydrogen (CO_2, CO, N_2, H_2O, CH_4), are used. In recent years, research on the development of new composite (block) sorption-active materials (CSAM), the advantages of which over granular adsorbents are low aerodynamic resistance, high strength, lower binder content, increased service life, has been actively carried out [39-42].

The latest advances in the design of PSA units allow implementing a “high-speed” PSA technological process while achieving a high purity degree of the product gas (for hydrogen – 99.99 vol.%, for oxygen – up to 95 vol.% and higher, for nitrogen – 99.99 vol.%), adjustable cycle speed, minimum time to set the unit into operation (cyclic steady state) regime, low consumption rates of the gas mixture per product gas unit, which can significantly reduce the cost of electricity for compressor equipment. PSA units are autonomous, mobile, reliable and the most profitable for consumers who use products of gas mixture separation irregularly in time [4].

The analysis of literature resources show that despite the rapidly increasing number of works in the field of cyclic adsorption processes and gas mixture separation units, the creation of industrial samples of such units is constrained by the problem of insufficiently complete knowledge of the properties and operation regimes of PSA units, imperfection of the equipment and technological design of cyclic adsorption processes from the point of energy and resource saving technologies, methodology for creating and researching resource-saving cyclic adsorption processes and units for gas mixture separation and purification, algorithmic and information support for their optimal design in conditions of uncertainty in the source data.

Modern means and methods for designing cyclic technological processes and units for gas mixture adsorption separation include the methods of chemical engineering processes and devices, system analysis, mathematical modeling and optimization (flexibility) theory, which, along with the intensively developing computer technology, make it possible to create efficient energy and resource-saving chemical engineering processes and units under conditions of uncertainty in the source data [43-46].

The aim of the paper is to generalize scientific achievements and improve the theoretical foundations and research methodology of resource-saving cyclic adsorption processes and units for separating multicomponent gas mixtures. The analysis and systematization of existing models and methods of mathematical modeling, optimization approaches and algorithms for the design of PSA units for hydrogen, oxygen and nitrogen extraction from gas mixtures are proposed; a comparative assessment of the effectiveness and feasibility of the proposed approaches is given; as well as the prospects and directions of further work in the field of mathematical modeling and optimal design of adsorption gas separation units are evaluated.

As a result, the task of creating such a “design” of an adsorption separation and purification unit for gas mixtures will be formalized. Heuristic approaches and regular algorithms for its solution will be proposed to guarantee: 1) determination of the optimal value of a certain economic indicator (for example, the reduced costs of designing a PSA unit or the cost of producing product gas); 2) maintaining the operability of the PSA unit (meeting the requirements of the technological regulations) during its operation despite the use of inaccurate mathematical models and random changes in internal and external factors within the specified limits [43-46].

Construction of a mathematical model for gas mixture separation by the PSA method

The quality of the mathematical model (MM) is characterized by the following criteria: 1) complexity of constructing the model; 2) convenience / ease of using the model; 3) adequacy of the model [4, 47].

A quantitative measure of the first criterion can be the duration of MM construction which varies from several weeks to several years for different cyclic adsorption processes and systems. The ease of using the model can be assessed by the frequency of its application in computer modeling tasks for cyclic adsorption processes and systems, or by the cost of computing resources to obtain numerical solutions of the MM equations. The third criterion has a quantitative assessment, where the estimates of the root-mean-square error are located. One can suspect an almost linear dependency of the first and second criteria, but there are examples of the absence of such a relationship [47]. The ease of using MM and a decrease in its labor intensity will most likely reduce its accuracy [47].

The introduced MM quality criteria will be useful in making subjective decisions at various steps of its construction.

The procedure for constructing a mathematical model for multicomponent gas mixture separation and product gas extraction using the analytical method formula consists of the following five steps [3, 4, 47].

1. Obtaining the MM structure of multicomponent gas mixture separation and product gas extraction processes (or structural synthesis of MM).
2. Obtaining experimental data on the studied process using special laboratory units, in each of which an experiment is carried out to study a particular physicochemical process (such as diffusion, mass transfer, thermal conductivity, adsorption equilibrium, etc.) among the significant phenomena.
3. Determining the vector of parameters / coefficients of the mathematical model (or parametric synthesis of MM) based on the experimental data obtained in laboratory conditions.
4. Analyzing the MM adequacy for multicomponent gas mixture separation and product gas extraction processes.
5. Ensuring the MM adequacy for multicomponent gas mixture separation and product gas extraction processes.

MM equations for gas mixture separation by the PSA method

The general task of the mathematical description of obtaining valuable gases by the PSA method can be traced by the example of the adsorption dynamics which reflects the general laws and methods used to simulate transport processes in the porous medium of the adsorbent [4]. The dynamics of adsorption processes considers the space-time distribution of components between the gas and solid phases and takes into account the following main aspects of this complex physical phenomenon: the balance of substances in the process of their movement and distribution in the adsorbing medium, kinetics and statics of substances adsorption, hydrodynamics of the process, the relationship between the thermodynamic parameters of the medium state, heat balance and heat transfer during adsorption in the moving medium [1-4, 47].

The following can be considered as possible options for the formation of MM structures:

1) spatial dimension of the task (one-dimensional 1D, two-dimensional 2D, three-dimensional 3D);

2) multicomponent gas mixture (binary, 3-component, multicomponent);

3) operation regime of the technological process or unit (statics or dynamics);

4) properties of the technological process (linearity / nonlinearity of adsorption-desorption isotherms; coincidence/non-coincidence of branches of adsorption and desorption isotherms; concentration / distribution of coordinates);

5) acceptance of the following physicochemical phenomena as significant / insignificant: diffusion of components in the gas mixture flow; mass transfer between the gas phase and the adsorbent; mass conductivity in the solid phase; thermal conductivity in the moving gas phase; heat transfer between the gas phase and the adsorbent; adsorption and desorption of gas mixture components on the surface and in the adsorbent micropores with the heat release; external/internal / mixed diffusion resistance has a limiting effect on the adsorption kinetics of gas mixture components.

By introducing the appropriate assumptions and choosing the desired operation regime, certain properties, mandatory physicochemical phenomena from the physicochemical model, it is possible to construct a number of MM structures of the technological process for multicomponent gas mixture separation and product gas extraction, which include equations of the component-wise material balance, sorption kinetics, heat balance, and conservation of momentum [1-4, 9-30].

In most works, it is assumed that the mixture flow of adsorbed substances inside the porous medium is carried out only in one (axial) direction [1-6, 11-31, 33-38, 46, 47].

In this case, the component-wise material balance equation looks as follows [4, 47]:

$$\frac{\partial c_k(z,\tau)}{\partial \tau}+\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial a_k(z,\tau)}{\partial \tau}+\frac{\partial\left(c_k v_g\right)}{\partial z}= \\ =D_{l,k}\frac{\partial^2 c_k(z,\tau)}{\partial z^2},\ k=1,2,3,\dots, \quad (1)$$

where $c_k -$ molar concentration of the k-th gas mixture component; $a_k -$ adsorption value of the k-th gas mixture component; ν_g – gas flow rate; $\tau -$ time, $\tau \in [0,\tau_{ads}]$, $\tau_{ads} -$ duration of the adsorption step; $z -$ spatial coordinate along the height (length) of the adsorbent bed, $0 \le z \le L$, L – height (length) of the adsorbent bed; $\varepsilon -$ porosity of the adsorbent bed; $D_{l,k} -$ effective coefficient of longitudinal diffusion of the k-th gas mixture component.

It should be noted that the operation of the PSA units during gas mixture separation and product gas extraction is carried out in a static regime – the Cyclic Steady State (CSS) regime [47] which is reached after a certain number of cycles (their number can reach several tens). The calculation of the CSS regime is carried out by solving the mathematical model equations of the dynamics of the PSA process over the time interval $[0, t_{css}]$, where $t_{css} = n\,\tau_c$, τ_c is the "adsorption-desorption" cycle time, and n is the number of cycles.

To describe the kinetics of the mass transfer process of the k-th gas mixture component with the adsorbent, it is necessary to carry out experimental studies and obtain experimental kinetic curves to substantiate the mass transfer region (external, internal, mixed diffusion) and determine mass transfer coefficients and mass conductivity in the porous medium of the adsorbent.

If external diffusion resistance has a limiting effect on the adsorption kinetics of the gas mixture components, then the kinetic equation is written as follows [4, 48]:

$$\frac{da_k}{d\tau} = \beta_{\mathrm{mt},k}(\mathrm{c}_k - \mathrm{c}_k^*), \qquad (2a)$$

where $\beta_{\mathrm{mt},k}$ – coefficient of external mass transfer of the k-th gas mixture component with the adsorbent, per unit of the adsorbent volume; c_k – current concentration of the k-th component in the gas mixture flow; c_k^* – concentration of the adsorptive on the interface equilibrium with the current value of adsorption a_k.

The most commonly used form of the kinetic equation is the formula in which the driving force of the intradiffusion adsorption process is written as the difference in the adsorbate concentration in the solid phase, known as the Gluckauf formula [4, 47]:

$$\frac{da_k}{d\tau} = \beta_{\mathrm{kin,k}}(a_k^* - a_k), \qquad (2b)$$

where a_k^* – adsorption value of the k-th component, which is equilibrium with the current concentration of the adsorptive in the flow c_k on the outer surface of the granules; $\beta_{\mathrm{kin,k}}$ – coefficient of mass conductivity (kinetic coefficient) of the k-th component in the porous medium of the adsorbent.

When describing the kinetics of the mixed diffusion process for multicomponent gas mixture separation and product gas extraction, either formula (2a) or (2b) is usually used with a general mass transfer coefficient β_0 which is the reciprocal of the total resistance in the system (consistinng of external and internal mass transfer resistances) [4 , 47]. The PSA models, which use the equations of component-wise material balance (1) and kinetics (2b), are known as the linear driving force (LDF) model [47].

The Langmuir, Freundlich and Langmuir – Freudlich isotherms are used to describe the phase equilibrium in the “gas – adsorbent” system in the PSA processes for extracting oxygen, nitrogen, and hydrogen from multicomponent mixtures [2, 6–31, 33–38, 49–51]. For example, the Langmuir – Freundlich equation for a multicomponent gas mixture has the following form:

$$a_k^* = \frac{(b_{1,k} - b_{2,k}T_{\mathrm{g}})b_{3,k}\exp(b_{4,k}/T_{\mathrm{g}})c_k^{(b_{5,k}+b_{6,k}/\mathrm{T_g})}}{1+\sum_j b_{3,j}\exp(b_{4,j}/T_{\mathrm{g}})c_j^{(b_{5,j}+b_{6,j}/\mathrm{T_g})}} \qquad (3a)$$

where b – vector of isotherm parameters; T_{g} – temperature of the gas phase in the adsorbent bed.

A brief overview of these isotherms is given in [4].

When modeling the PSA processes, the Dubinin-Radushkevich-Astakhov (DRA) equations obtained according to the theory of volumetric filling of micropores developed by the Soviet academician M.M. Dubinin's are used along with the Langmuir isotherm equation [13, 52-54]:

$$a_k^* = \frac{W_0}{\mathrm{V}_k^*}\exp\left[-\left(\frac{RT_{\mathrm{g}}\lg\left(\frac{P_{\mathrm{sat},k}}{P_k}\right)}{\varphi_k E}\right)^n\right], \qquad (3b)$$

where W_0 – limiting adsorption volume, cm^3/g; V_k^* – molar volume of the k-th component, cm^3/mmol; E – characteristic adsorption energy, J/mol; φ_k – coefficient of affinity of the k-th component to the standard gas; $P_{\mathrm{sat},k}, P_k$ – saturation pressure and partial pressure of the k-th component in the gas mixture; n – exponent of the DRA equation [55].

Since the velocity ν_{g} and the density ρ_{g} of the gas flow change during the adsorption of gas components, the equation of the gas flow hydrodynamics in the granular adsorbent bed is written as follows [56]:

$$\frac{\partial(\nu_{\mathrm{g}}(z,\tau)\rho_{\mathrm{g}})}{\partial x} + \rho_{\mathrm{a}}\frac{\partial\sum_k a_k}{\partial\tau} + \frac{\partial\rho_{\mathrm{g}}}{\partial\tau} = 0, \qquad (4)$$

where ρ_{a} – bulk density of the adsorbent.

To take into account the change in pressure in the adsorbent bed due to aerodynamic drag, the Ergun equation is used [57]:

$$\frac{\partial P(z,\tau)}{\partial z} = -\left(\frac{150(1-\varepsilon)^2}{(d_{\mathrm{gr}}\varsigma)^2\varepsilon}\mu_{\mathrm{g}}\nu_{\mathrm{g}} + 1.75M_{\mathrm{g}}\rho_{\mathrm{g}}\frac{(1-\varepsilon)}{d_{\mathrm{gr}}\varsigma\varepsilon^3}\nu_{\mathrm{g}}^2\right) \qquad (5)$$

where P – pressure of the gas mixture; ς – sphericity coefficient of adsorbent granules; μ_{g} – dynamic viscosity of the gas mixture; M_{g} – molecular weight of the gas mixture; R – universal gas constant; d_{gr} – equivalent adsorbent grain (granule) diameter.

The relationship between the current values of pressure P, temperature T_{g} and density ρ_{g} of the gas mixture is carried out through the equation of an ideal gas state [47].

The heat balance equation for the elementary volume of the granular layer in shape is drawn up similarly to the material balance equation, while for the adiabatic process, the heat balance equation for the gas phase can be written as follows [4]:

$$\mathrm{c}_p^{\mathrm{g}}\rho_{\mathrm{g}}\frac{\partial T_{\mathrm{g}}(z,\tau)}{\partial\tau} + \alpha_{\mathrm{hd}}S_{\mathrm{gr}}\left(T_{\mathrm{g}}(z,\tau) - T_a(z,\tau)\right) + \\ + \mathrm{c}_p^{\mathrm{g}}\rho_{\mathrm{g}}\nu_{\mathrm{g}}\frac{\partial T_{\mathrm{g}}(z,\tau)}{\partial z} = \lambda_{\mathrm{g}}\frac{\partial^2 T_{\mathrm{g}}(z,\tau)}{\partial z^2}, \qquad (6)$$

where T_a – current temperature of the adsorbent granules; $\mathrm{c}_p^{\mathrm{g}}$ – specific volumetric heat capacity of the gas mixture; λ_{g} – coefficient of thermal conductivity of the gas phase; α_{hd} – coefficient of heat transfer from the gas mixture to adsorbent granules; S_{gr} – coefficient of the specific surface area of an adsorbent granule with an equivalent diameter d_{gr}.

In a number of works [2, 11, 31], heat losses through the adsorber wall are also taken into account. For this purpose, an additional term in equation is used (6):

$$\frac{4\alpha_{\text{w}}}{D_{\text{int}}}\left[T_{\text{g}}(x,\tau) - T_{\text{env}}\right],$$

where α_{w} – coefficient of heat transfer through the adsorber wall; D_{int} – inner diameter of the adsorber; T_{env} – ambient temperature.

Heat exchange between the solid and gas phase flow is limited either by external heat transfer or by thermal conductivity of granules, or determined by both two mechanisms. In real operating conditions of granular adsorbent beds, heat exchange, in contrast to mass exchange, is almost completely determined by heat transfer from the flow core to the outer surface of solid particles. The heat propagation through the particle occurs rather quickly and, taking this into account, the heat transfer equation can be written in the following form [4]:

$$\alpha_{\text{hd}} S_{\text{gr}}\left(T_{\text{g}}(z,\tau) - T_a(z,\tau)\right) + \\ + \sum_{k=1}^{K} \Delta h_k \frac{\partial a_k}{\partial \tau} = c_p^a \rho_a \frac{\partial T_a(z,\tau)}{\partial \tau}, \quad (7)$$

where c_p^a – specific heat of the adsorbent; Δh_k – adsorption heat of the k-th gas mixture component.

The presented model equations of the processes in the PSA adsorber (1) - (7) are a system of 1D partial differential equations (PDE) supplemented by the corresponding initial and boundary conditions set for each step of the PSA process cycle (adsorption, desorption, pressure equalization, etc.) [2, 6, 12, 33, 47, 52]; boundary and initial conditions interconnect the flows coming from one adsorber to another during the full cycle of the PSA process.

The known values of gas concentrations and temperatures in the first cycle are used as initial conditions. On subsequent cycles, the initial values are the profiles along the height of the adsorbent bed obtained at the previous step at the final time $\tau = \tau_{\text{ads}}$ or $\tau = \tau_{\text{des}}$ [2, 6, 12, 33, 47, 52]. The specified values of concentrations, temperatures, pressures, flow rates are used as boundary conditions at the adsorber inlet (at $z = 0$) in the form of constants or known functions of time; at the adsorber outlet (at $z = L$), the Dankvert's conditions are used [2, 6, 12, 33, 47, 52].

Next, the model equations of the technological scheme elements using the example of gas mixture separation in a 2-bed adsorber PSA unit should be considered (Fig. 1) [2, 52].

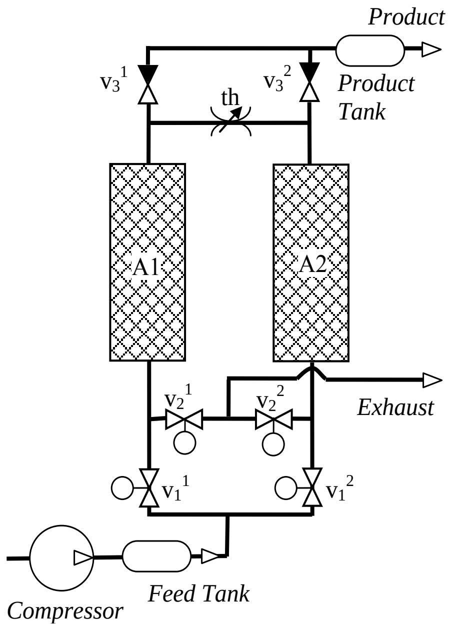

Fig. 1. Technological scheme of a 2-bed adsorber PSA unit: A1,A2- adsorbers; v_i^j, i=1,2, j=1,2 - intake and exhaust control valves; v_3^1, v_3^2 – check valves; th- throttle

Рис. 1. Технологическая схема двухадсорберной установки КБА: A1,A2- адсорберы; v_i^j, i=1,2, j=1,2 - впускные и выпускные управляющие клапаны; v_3^1, v_3^2 – обратные клапаны; th- дроссель

The dynamics of pressure change at the adsorber inlet of the PSA unit is described by the following ordinary differential equations:

$$\frac{dP_{\text{ads}}^{\text{in}}(\tau)}{d\tau} = K_{\text{ads}}\left(P_{\text{comp}} - P_{\text{ads}}^{\text{in}}(\tau)\right), \quad (8)$$

$$\frac{dP_{\text{des}}^{\text{in}}(\tau)}{d\tau} = K_{\text{des}}\left(P_{\text{des}}^{\text{in}}(\tau) - P_1^{\text{out}}\right), \quad (9)$$

where $K_{\text{ads}}, K_{\text{des}}$ – empirical coefficients; P_{comp} – pressure generated by the compressor; P_1^{out} – ambient pressure (P_1^{out} – pressure created by the vacuum pump, if there is a vacuum pump in the circuit).

The flow rates of the gas mixture passing through the intake G_{in}, exhaust G_{ex} control valves are calculated using the following formulas:

$$G_{\text{in}}(\tau) = K_{\text{V}}^{\text{in}} \psi^{\text{in}} (P_{\text{comp}} - P_{\text{ads}}^{\text{in}}(\tau)), \quad (10)$$

$$G_{\text{ex}}(\tau) = K_{\text{V}}^{\text{ex}} \psi^{\text{ex}} \left(P_{\text{des}}^{\text{in}}(\tau) - P_1^{\text{out}}\right), \quad (11)$$

where $K_{\text{V}}^{\text{in}}, K_{\text{V}}^{\text{ex}}$ – capacity of intake and exhaust valves; $\psi^{\text{in}}, \psi^{\text{ex}}$ – opening degrees of intake and exhaust valves, $\psi^{\text{in}} \in [0;1]$, $\psi^{\text{ex}} \in [0;1]$; at $\psi = 0$ the valve is closed, ar $\psi = 1$ the valve is fully open [28].

The flow rate through the throttle G_{th} can be calculated in two ways. According to the first method, the coefficient θ of the reverse and forward flow ratio is used [13, 52]:

$$G_{\text{th}}(\tau) = \theta\, G_{\text{ads}}^{\text{out}}(L,\tau) \frac{P_{\text{des}}^{\text{in}}(\tau)}{P_{\text{ads}}^{\text{out}}(\tau)}, \quad (12a)$$

where $G_{\text{ads}}^{\text{out}}$ – flow rate of the gas mixture at the adsorber outlet, $P_{\text{ads}}^{\text{out}}(\tau) = P(L,\tau)$ – pressure at the adsorber outlet at the adsorption step.

In the second method, the throttle diameter d_{th} is used to calculate the flow rate, and the effect of "blocking" the gas flow is taken into account, when a further decrease in the adsorber pressure does not affect the flow rate, and the gas velocity in the throttle reaches the speed of sound [18]:

$$G_{\text{th}} = 1.268 \cdot 10^5 \cdot P_{\text{ads}}^{\text{out}}\, d_{\text{th}}^2 T^{-1/2} \lambda \left(1 - \frac{1}{6}\lambda^2\right)^{5/2}, \quad (12b)$$

where the parameter λ is calculated as follows:

$$\lambda = \left(6\left[1 - \left(P_{\text{des}}^{\text{in}}/P_{\text{ads}}^{\text{out}}\right)^{2/7}\right]\right)^{1/2}.$$

This formula is valid for the gas mixture flow with an adiabatic exponent of 1.4 and $\lambda < 1$, which corresponds to the value $P_{\text{des}}^{\text{in}}/P_{\text{ads}}^{\text{out}} > 0.528$.

When the value $P_{\text{des}}^{\text{in}}/P_{\text{ads}}^{\text{out}}$ decreases to 0.528, the effect of "blocking" the gas flow occurs. For this reason, at $P_{\text{des}}^{\text{in}}/P_{\text{ads}}^{\text{out}} \leq 0.528$, it is assumed that $\lambda = 1$ and the formula for calculating the gas flow rate G_{th} through the throttle takes the following form:

$$G_{\text{th}} = 1.268 \cdot 10^5 \cdot P_{\text{ads}}^{\text{out}}\, d_{\text{th}}^2 T^{-1/2} \left(\frac{5}{6}\right)^{5/2}. \quad (12c)$$

The capacity of the PSA unit is estimated from the flow rate of the gas mixture at the unit outlet at the current value of the product gas concentration at the adsorber outlet [2, 18, 19, 28-31, 33-38, 46, 51, 58]:

$$G^{\text{out}} = G_{\text{ads}}^{\text{out}} - G_{\text{th}}. \quad (13)$$

The degree of product gas extraction is calculated by the formula [2, 18, 19, 28-31, 33-38, 51, 58]:

$$\eta = \frac{c^{\text{out}} G^{\text{out}}}{c^{\text{in}} G^{\text{in}}} 100\%, \quad (14)$$

where $c^{\text{in}}, c^{\text{out}}$ – product gas concentration at the adsorber inlet and outlet; G^{in} –flow rate of the gas mixture at the adsorber inlet, G^{out} – unit productivity.

The dynamics of changes in the pressure and concentration of the product gas in the receiver is described by the following differential equations:

$$\frac{dP_{\text{res}}(\tau)}{d\tau} = K_{\text{res}}\left(P_{\text{ads}}^{\text{out}}(\tau) - P_{\text{res}}\right), \; P_{\text{res}}(0) = P_{\text{res}}^0, \quad (15)$$

where K_{res} – empirical coefficient, $P_{\text{ads}}^{\text{out}}$ – pressure at the adsorber outlet; P_{res} – pressure in the receiver.

$$\frac{dc_{\text{res}}(\tau)}{d\tau} = \frac{G^{\text{out}}}{V_{\text{res}}}\left(c^{\text{out}}(\tau) - c_{\text{res}}\right), \; c_{\text{res}}(0) = c_{\text{res}}^0. \quad (16)$$

where V_{res} – receiver capacity; $c^{\text{out}} = c(L,\tau)$ and c_{res} – product gas concentrations at the adsorber outlet and in the receiver, respectively.

The sequence of solving the system of equations of the mathematical model (1)-(16) of the PSA unit dynamics is presented in the form of a diagram in Fig. 2.

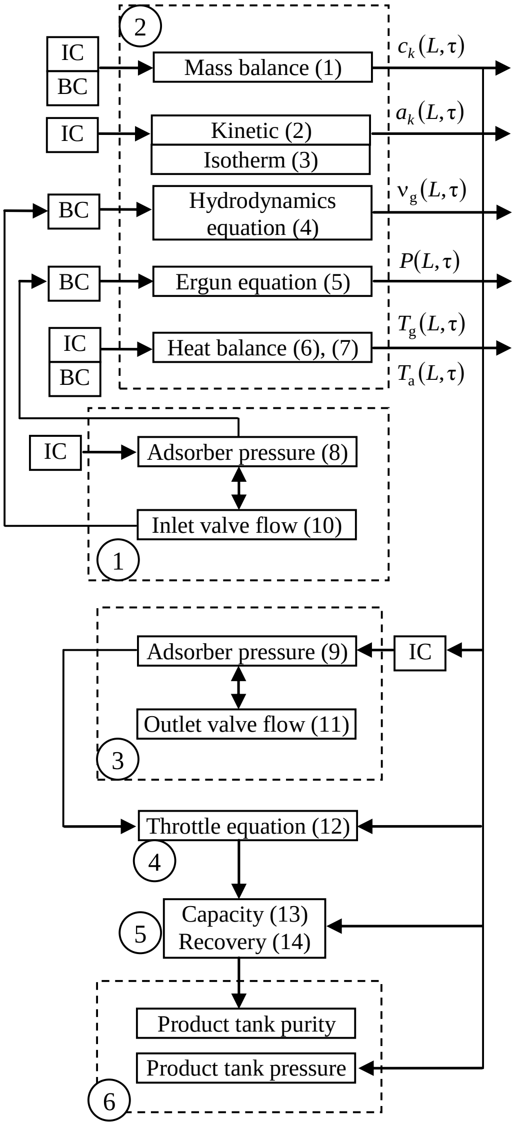

Fig. 2. The sequence of solving the mathematical model equations for the two-adsorber PSA unit at the adsorption step: IC – initial conditions, BC – boundary conditions

Рис. 2. Последовательность решения уравнений математической модели двухадсорберной установки КБА для стадии адсорбции: Н.У. – начальные условия, Г.У. – граничные условия

The mathematical model obtained using the analytical method formula for constructing models contains a lot of information about the design and operation principles of the technological process of multicomponent gas mixture separation and product gas extraction, as well as the characteristics of the physicochemical phenomena occurring in it. This circumstance allows using analytical models for solving various problems of designing equipment and technological devices, performing technological and design calculations, production automation, etc.

The analysis of the mathematical models used to describe the processes of gas mixture separation and oxygen, nitrogen and hydrogen extraction by the PSA method shows that most researchers use various assumptions regarding the accounting / neglecting certain physicochemical phenomena for MM construction, which leads to different sets of differential and finite equations.

When formulating the problems of the sorption dynamics in order to simplify the task, and in some cases this simplification is close to real conditions, the sorption kinetics is neglected assuming that the adsorption equilibrium is established almost instantaneously. Then, instead of the sorption kinetics equation, equations of sorption isotherms will be included in the system of MM differential equations of sorption dynamics. In accordance with this remark and the accepted assumptions, MM can be classified into equilibrium and nonequilibrium [2, 6, 11, 12, 14, 18-31, 33-38, 47]; external, internal and mixed diffusion [2, 6, 11, 12, 14, 18-31, 33-38, 47]; isothermal [18, 34, 35] and non-isothermal (taking into account the heat effects of adsorption and desorption, and the corresponding change in temperature in the adsorbent and the gas phase) [2, 6, 11, 12, 18, 33, 36-38, 47].

Equilibrium models are mainly used to study, in the first approximation, the properties and operation regimes of the PSA processes and units when separating gas mixtures and releasing target gases [47].

The most widely used mathematical model is one that describes the cyclic processes of gas mixture adsorption separation in the external diffusion region by linear differential equations with partial and ordinary derivatives (1) and (2b) (linear driving force model – LDF). In works [2, 6, 11, 12, 14, 18-31, 33-38, 47], it is shown that the LDF model satisfactorily describes the PSA processes for air and synthesis gas separation when obtaining high purity gases, i.e. before a sharp decrease in the gas concentration at the adsorber outlet caused by the exhaustion of the adsorption capacity of the adsorbent by sorbed components. In this case, the use of more complex PSA models describing the course of cyclic adsorption-desorption processes, for example, in the mixed-diffusion region, leads to an insignificant refinement of the calculation results, but requires a significant increase in processing time for calculations [47]. In [4], it is noted that the LDF mathematical model with a fairly correct and accurate determination of the kinetic parameters is most often used to describe the majority of cyclic processes of adsorption separation of multicomponent gas mixtures.

Isothermal LDF models are usually used for small-sized PSA units for air oxygen enrichment [18]. This is due to the fact that in such units temperature fluctuations in the adsorption – desorption process are very insignificant, ~ 5 °C. PSA units for hydrogen extraction are significantly superior to PSA oxygen units in terms of size, cycle duration and thermal effects during the adsorption of gases accompanying hydrogen (CO_2, CO, CH_4); therefore, non-isothermal models are often used for their calculations [2, 10, 27-31, 33].

Determination of the mathematical model coefficients

The mathematical model equations (1)-(16) of gas mixture adsorption separation by the PSA method include kinetic coefficients of mass transfer $\beta_{\mathrm{mt},k}$, $\beta_{\mathrm{kin},k}$ of the extracted gas mixture components, heat transfer α_{hd}, longitudinal mixing $D_{l,k}$ of the gas phase in the porous medium of the adsorbent, etc., the determination of which according to the experimental data is associated with the solution of a laborious and often incorrect inverse coefficient problem.

The simplest approach to determining the coefficients of the model equations in the first approximation is using criterion dependencies known from scientific resources [1, 4, 47]. In fact, the model parameters depend on the current values of the transfer potentials (concentration, temperature and pressure in the system) of the gas mixture components which change during the gas mixture adsorption separation process [21, 51].

A more complex approach consists in determining the parameters of the mathematical model in the form of functional dependencies on the transfer potentials according to experimental kinetic curves by solving a regularized inverse coefficient problem [59, 60]. According to this approach, to determine mass transfer coefficients $\beta_{\mathrm{mt},k}$, $\beta_{\mathrm{kin},k}$ in the first approximation, criterion equations [4] are used, and their refinement is carried out according to the experimental kinetic curves in the first ($\beta_{\mathrm{mt},k}$) and second ($\beta_{\mathrm{kin},k}$) adsorption (desorption) periods, respectively.

In many works on the mathematical modeling of cyclic processes of gas mixture adsorption separation, a criterion equation is used in order to calculate the average coefficient of mass conductivity over the entire range of concentrations of the distributed substance in the solid phase [1, 4, 14, 20, 23, 33, 47]:

$$\beta_{\mathrm{kin},k} = 15\frac{D_{\mathrm{ef},k}}{r_{\mathrm{gr}}^2},$$

where $D_{\mathrm{ef},k}$ – effective diffusion coefficient, including Knudsen diffusion mechanism, molecular diffusion mechanism and tortuosity of pores; r_{gr}– radius of the adsorbent particle.

As a rule, $D_{\mathrm{ef},k}$ is calculated using the Bosanquet equation [32, 33]. Currently, there is no single approach to calculating $D_{\mathrm{ef},k}$; for the same gases and adsorbents, different authors use different methods for its calculation [1, 4, 14, 20, 23, 33, 47].

To calculate the coefficient of longitudinal mixing D_l of the gas mixture in the porous medium of the adsorbent, a formula of the following form [1, 4, 14, 20, 23, 33, 47] is usually used:

$$D_l = 0.7D_{\mathrm{md}} + 0.5\nu_{\mathrm{g}}d_{\mathrm{gr}},$$

where D_{md} – molecular diffusion coefficient calculated by the Fuller – Schletter – Giddings formula [14, 55]:

$$D_{\mathrm{md}} = \frac{10^{-3}T_{\mathrm{g}}^{1.75}\sqrt{\sum_k M_{\mathrm{g},k} / \prod_k M_{\mathrm{g},k}}}{P\left(\sum_k {V_k}^{1/3}\right)^2},$$

where V_k – diffusion volumes.

The Fuller – Schletter – Giddings formula is considered to be quite reasonable for calculating the coefficient D_{md} and often used in works on mathematical modeling of cyclic processes of gas mixture adsorption separation, which take into account the longitudinal mixing of the gas phase in the porous medium of the adsorbent [1, 4, 14, 20, 23, 33, 47].

The inertia of thermal processes in the adsorber and the high thermal conductivity of the adsorbent lead to diffuse thermal fronts (as opposed to “steep” concentration fronts). This leads to the “averaging” of the heat amount over the height of the adsorbent bed and a decrease in the requirements for the accuracy of describing heat transfer processes in contrast to mass transfer processes [47]. In this regard, in order to calculate the average heat transfer coefficient over the entire temperature range in the solid phase, the criterion equation of the following form [61] is most often used:

$$\alpha_{\mathrm{hd}} = \frac{\lambda_{\mathrm{g}}\mathrm{Nu}}{d_{\mathrm{gr}}},$$

where Nu – Nusselt criterion, d_{gr} – equivalent grain (granule) adsorbent diameter; λ_{g} – coefficient of thermal conductivity of the gas phase.

To calculate the adsorption separation process for the gas mixture that occurs in the mixed diffusion region, data on the coefficients of mass transfer and mass conductivity of the adsorptive components in the porous medium of the adsorbent are required. In [59], a method for determining the coefficients $\beta_{\mathrm{kin},k}$ and $\beta_{\mathrm{mt},k}$ from the experimentally obtained kinetic curves, which can be adapted for the PSA gas separation processes, is presented. This technique consists in splitting the kinetic absorption curve of the corresponding component into two periods: in the first period, the adsorption process is limited by external diffusion; in the second period, by internal diffusion. The critical point which delimits the first and second periods is visually determined on the kinetic curve. In the first period of kinetics (up to the critical point on the kinetic curve), the rate of the process is constant, and a constant concentration c^* of the adsorptive is maintained at the granule surface. In the first period of kinetics $a(z) \approx \bar{a}$, the intensity of the internal mass transfer is high enough to maintain the saturation concentration in the external phase near the granule surface. At the critical point, the second period of kinetics begins, in which the concentration of the adsorptive at the granule surface becomes greater than c^*, and at $\tau \geq \tau_{\mathrm{cr}}$ (τ_{cr} is the time to reach the critical mass content) it is determined by the phase concentration equilibrium function [59]. Further, according to the method [59], the mass transfer coefficient for the first period $\beta_{\mathrm{mt},k}$ and the dependency of the mass conductivity coefficient $\beta_{\mathrm{kin},k}(a)$ for the second period are determined.

Mathematical modeling of the gas mixture separation processes by the PSA method

It was noted earlier that the operation of the PSA units during gas mixture separation and product gas extraction is carried out in the CSS regime, the calculation of which is carried out by solving the mathematical model equations for the dynamics of the PSA process over the time interval $[0, t_{\mathrm{css}}]$. The CSS regime is considered achieved if a condition of the form [11, 12, 18-20, 23-29, 47] is fulfilled:

$$|c_n^{\mathrm{out}}(\tau_{\mathrm{ads}}, L) - c_{n-1}^{\mathrm{out}}(\tau_{\mathrm{ads}}, L)| \leq e, \qquad (17)$$

where c^{out} – product gas concentration at the adsorber outlet; e – small positive number, for example $e = 10^{-3}$ [47]; n – cycle number.

The number of cycles required for the onset of the CSS regime is usually ~ 10-15 for the air separation process and ~ 5-10 for the synthesis gas separation process (in some cases, the number of cycles can reach several tens) [11, 12, 28, 49]. On productive workstations, the time to reach the CSS regime for medical concentrators is ~ 1-2 min, for industrial units ~ 10 min [11, 12, 18, 19, 28]. Thus, the calculation of the CSS regime requires large expenditures of computational resources, which is especially critical when solving the optimization problems of operation regimes and optimal design of PSA units [47].

The presence of “steep” adsorption fronts in the adsorbent bed and the nonlinearity of the system of the mathematical model differential equations for the gas mixture adsorption separation process (1)-(16) make it difficult to obtain only one solution due to the possible instability of the direct problem [47]. Historically, in order to solve partial differential equations, approximate analytical methods have been developed: separation of variables, integral transformations (methods of Laplace, Fourier, Hankel, etc.), Green's functions, variational method and others. In all these methods, the direct problem under study is transformed into some other (also rather laborious) problem, the solution of which is used in construction of an approximate solution of the original problem.

Numerical methods are based on the theory of difference schemes or finite elements reducing a differential problem to a system of algebraic / finite difference schemes (explicit and implicit), which are different for different types of partial differential equations and even for different problem statements. Further, an algorithm for solving the direct problem is developed using an explicit or implicit difference scheme, and a software implementation of the algorithm is created. Not all of these algorithms provide the absolute stability of the difference problem solution; in particular, many explicit difference schemes turn out to be conditionally stable only for certain parameters of the difference grid. Implicit difference schemes used to solve stiff equations turn out to be absolutely stable, but at the same time more laborious.

One of the effective methods for solving the equations of the PSA model is the method of lines implementing a two-step procedure [47]. At the first step, using algebraic / finite difference schemes the system of partial differential equations with respect to the spatial coordinate is transformed into a system of ordinary differential equations along a given family of lines with initial and boundary conditions. The system of ordinary differential equations obtained in this way can be solved by the 4th-order Runge-Kutta method with automatic step selection. The method of lines has an acceptable practical accuracy and convergence rate, which makes it the most preferable method for solving the equations of the mathematical model (1) - (16) with initial and boundary conditions.

In order to avoid obtaining unstable finite-difference schemes that lead to disturbances (oscillations) in adsorption profiles, a number of methods have been proposed for constructing highly efficient finite-difference schemes. In particular, in [19], the formation of a finite-difference scheme based on the theory of wavelets is proposed. In [62], it is proposed to use the backward differentiation formula (BDF) to approximate the system of the mathematical model differential equations for extracting hydrogen from the gas mixture by the PSA method; in [20], the Differential Quadrature Method is used to solve the system of MM differential equations for air oxygen enrichment by the VPSA method; in [23], an original numerical-analytical method for constructing computational grids and choosing the centers of radial-basis functions is proposed, which is capable of adapting to the properties of the boundary value problem and characterized by high processability and low computational costs.

One of the effective approaches to obtaining stable algebraic difference approximation schemes are flux limiters, which make it possible to almost completely eliminate disturbances in the resulting adsorption profiles [47]. The most commonly used flux limiters are superbee, Van Leer, and minmod [47]. The flux limiter is a function (large or identically equal to zero) which is added to each time derivative included in the system of ordinary differential equations obtained as a result of approximating the original system (1) - (16) in the spatial coordinate along the family of lines. With abrupt changes in the gradient or zero gradient of the differential equation solution, the flux limiter function is identically equal to zero and the approximation is performed by a difference scheme with low resolution; in the case of a smooth solution, the flux limiter function is identically equal to one and the approximation is performed by a high-resolution scheme.

Most authors use the method of lines to solve the differential equations of the mathematical model for the gas mixture adsorption separation process in the MatLab software environment. The system of ordinary differential equations obtained in the course of the approximation is solved using the ode15s [27] or ode23tb [26] solvers designed to solve stiff differential equations with addition to the derivatives of the flux limiter functions. In particular, in [12], to solve the MM equations of the gas mixture separation processes by the PSA method, a version of the Van Leer flux limiter function is used with changes that ensure the continuity of the first derivatives of this function. In [6], in order to solve the mathematical model equations for the dynamics of the air oxygen enrichment process carried out in a medical oxygen concentrator by the VPSA method, the method of lines is also used, and the resulting system of ordinary differential equations is solved using the DASOLV solver in the gPROMS software package. A similar approach is used in [63, 64] for mathematical modeling of the technological process of synthesis gas separation and hydrogen extraction by the PSA method.

When solving the mathematical models equations for cyclic processes of gas mixture adsorption separation, high efficiency (absence of disturbances in the adsorption and temperature profiles, high speed of response when setting the PSA unit to the CSS regime) is achieved using solvers of the Aspen Adsorption, Comsol Multiphysics, Ansys Fluent software products designed to solve mathematical physics problems. In particular, Comsol Multiphysics is used in [15, 50, 65, 66] to simulate multi-adsorber PSA and VPSA units for hydrogen, nitrogen and oxygen extraction from multicomponent gas mixtures; in works [2, 7, 14, 36, 67–69] Aspen Adsorption is used.

In recent years, the methods of computational fluid dynamics (CFD modeling) have become a promising area of research into the processes of mass and heat transfer in the technological process of gas mixture separation by the PSA method. The development of CFD modeling methods is due to the relative availability of high-performance computers, as well as specialized software for CFD modeling, such as Comsol Multiphysics and Ansys Fluent.

With the use of computational fluid dynamics methods and CFD modeling software, it is possible to use 2D and even 3D mathematical models for solving problems which are inaccessible when using 1D models, in particular [70-76]:

- computer simulation of the gas mixture separation processes in adsorbers with radial or spiral directions of the gas flow, taking into account the unevenness of its distribution in the porous medium of the adsorbent, stagnant zones and an adequate assessment of the decrease in the dynamic capacity of the adsorbent;
- modeling of processes in adsorbers filled with adsorbents with a complex shape of granules (cuttings, tablets) or when using composite sorption-active materials (CSAM).

In a number of works, 2D adsorber models are used to study the properties and regimes of the designed PSA units [70-76]. Thus, in [73], it is established that: 1) the concentration and temperature in the adsorbent bed have a substantially non-uniform distribution, which negatively affects the kinetics and reduces the efficiency of adsorption-desorption processes in the adsorber; 2) a moderate pressure drop provides a uniform distributed flow and, accordingly, an increase in the performance of the PSA unit adsorber as a whole. In [70], a 2D model in Ansys Fluent 12.1 is used to study the effect of pressure, temperature, and flow rate on the efficiency of the gas mixture adsorption separation by the PSA method. In [75], the 2D model is used to study the properties and regimes of the designed RPSA units for air oxygen enrichment and to determine the promising designs of adsorbers. In [76], a VPSA scheme for the equipment and technological design of a medical oxygen concentrator with a pressure of 0.82 bar at the regeneration stage is proposed; the calculation of the dynamics of the technological process is implemented in the Comsol Multiphysics software environment using a 2D model of an oxygen generator. In [74], a 2D model of the PSA oxygen generator with radial flow movement is developed and investigated in the Ansys Fluent 16 software environment. In [72], it is shown that the difference in accuracy between 2D and 1D modeling of the adsorber for the air separation technological process by the PSA method with axial flow motion in the adsorbent bed is ~ 1-2%.

Finally, in [71], the study of the properties and regimes of the designed PSA units for gas mixture separation is carried out using a 3D model. It has been found that the most important (having the greatest sensitivity in relation to the performance criteria of the PSA units) parameters and regime (control) variables of the technological process for gas mixture adsorption separation are the coefficients of mass transfer and mass conductivity of the gas mixture components in the porous medium of the adsorbent, heat transfer of the adsorbent in the gas phase, thermal conductivity of the moving medium, cycle time, pressures at the adsorbent adsorption and regeneration steps, and the reverse flow coefficient. The efficiency of functioning and the accuracy of mathematical modeling for the dynamics of the technological process of gas mixture separation by the PSA method is also indirectly influenced by the adequate choice of equations (experimental determination) of adsorption-desorption isotherms and the hydrodynamic perfection of the gas flows organization in the bulk adsorbent bed (absence or presence of stagnant zones, flow slip, wall effect, etc.) [71].

Optimization of operation regimes and design of gas mixture separation units by the PSA method

When solving optimization problems of the operation regimes and design of the gas mixture adsorption separation and purification processes, the so-called indefinite (“inaccurate”) information about physicochemical parameters, characteristics of source / “raw” substances, design / geometrical parameters of technological equipment fragments, external operating conditions of production, financial / cost data, etc., is often used, which significantly affects the quality of the designed technological process characterized by known technical and economic indicators, for example, purity, degree of product gas extraction, production cost, profit and other indicators. A quantitative account of these “inaccurate”/random factors is the key point in the optimization and design of the technological process of gas mixture adsorption separation and purification under conditions of partial (incomplete) uncertainty.

The purpose of the optimal design of the PSA unit for gas mixture separation is to determine the optimal design from the point of any criterion (technological scheme equipment and technological design), i.e. the PSA process and the unit as a whole. The optimal "design" of the unit should guarantee the fulfillment of the design requirements (restrictions) associated with the provision of the required technical and economic indicators of the unit operation.

The optimization problems of the operation regimes and design parameters of PSA units for hydrogen, oxygen and nitrogen extraction are formulated and solved in the works of a number of scientists [5-7, 10-12, 18, 19, 24, 26, 28-31, 49, 52, 58, 63, 77-83]. The cited works considered multi-adsorber RPSA units [5, 7, 28-30, 49, 52, 78-83], VSA units [10, 12, 19, 77] and VPSA units [6, 11, 18, 26, 31, 58, 63] for oxygen, nitrogen and hydrogen extraction from gas mixtures with a capacity of up to 100 nm^3/h. Both industrial zeolites 13X [18, 52, 81], 5A [11, 82], LiLSX [6], activated carbons [5, 10, 30, 31, 49] (allowing to obtain oxygen with a purity of up to 95 vol.%, hydrogen with a purity of up to 99.99 vol.%, nitrogen with a purity of up to 99.9995 vol.%) and promising experimental sorbents AgLiLSX [24] and Ag-ETS-10 [26] with high selectivity for argon and allowing to obtain oxygen with a purity of up to 99.5 vol. % are used as adsorbents in these works, but the recovery rate is only ~ 27.3% and lower [24, 26].

Technical and economic performance indicators can be selected as a criterion for the optimal design of the technological process and the unit for gas mixture adsorption separation and purification, for example, the extraction degree (14) of the target product [12, 28, 31, 49, 52, 58, 78, 83]; reduced costs [63, 79]; profit from the operation of the PSA unit for a certain period of time [18]; energy consumption [6, 29]; unit productivity [6], etc. The calculation of the optimality criteria values is carried out by integrating partial differential equations describing the dynamics of the gas mixture adsorption separation and purification processes over the time interval $[0, \mathrm{t_{css}}]$. When designing industrial, oxygen, nitrogen and hydrogen units, optimization problems are formulated and solved using economic criteria [84].

Relationships in the formulation of optimization problems of operation regimes and optimal design of the technological process and the unit for gas mixture adsorption separation and purification by the PSA method are set by a system of differential equations (1)-(16), which are the balance equations of substances in the sorbing medium (differential equations with partial derivatives of a parabolic type), equations of the adsorption-desorption kinetics (ordinary differential equations), equations of adsorption-desorption isotherms (finite equations), equations of hydrodynamics (equations of continuity, motion and state of the gas mixture), the equation of balance and heat propagation in the moving medium (gas flow) and stationary medium (adsorbent) (partial differential equations), initial and boundary conditions for partial differential equations, and ordinary differential equations of the mathematical model [1-6, 11-31, 33-38, 46, 47]. Thus, the dynamics of the projected technological process and the unit for gas mixture adsorption separation and purification in time $\tau, 0 \leq \tau \leq \tau_c$ and in the spatial variable z is described by the system of differential and finite equations (1) - (16) with initial and boundary conditions representing in general form the nonlinear vector functional dependence $F(x,u,d,y,b) = 0$ of input (independent) coordinates ⟦$x = \{x_j, j = \overline{1,m}\} \in X$ and regime (control) variables $u = \{u_\mathrm{i}, i = \overline{1,n}\} \in U$ from bounded closed sets X, U of number spaces $\mathrm{E^m}$ and $\mathrm{E^n}, \mathrm{m} \leq \mathrm{n}$; output coordinates $\mathrm{y} = \{\mathrm{y_i}, \mathrm{i} = \overline{1,n}\} \in Y$ from the bounded open set Y of the number space E^n; design parameters (dimensions) $d = \{d_l, l = \overline{1,p}\} \in D$ of the technological equipment of the PSA unit from a bounded closed set D of the number space E^p; physicochemical parameters $b = \left\{b_\rho, \rho = \overline{1,r}\right\} \in B$ from the closed set B; $F(\cdot) = \{F_i(\cdot), i = \overline{1,n}\}$ is a vector function nonlinear in x, y twice continuously differentiable with respect to the arguments x, u, d, y and the parameter b [44].

Let us consider the arguments of the nonlinear vector function $F(\cdot)$ and their relationship in detail. The x coordinate can be represented in the form $x_{\text{н}}^{\text{p}} + \Delta x$, where $x_{\text{н}}^{\text{p}}$ is the specified load by the "raw material" on the technological process of gas mixture adsorption separation and purification, Δx is an uncertain alternate component such that $\|\Delta x\| < \left\|x_{\text{н}}^{\text{p}}\right\|$ or even $\|\Delta x\| \ll \left\|x_{\text{н}}^{\text{p}}\right\|$; vector parameter b can also be represented in the form $\bar{b} + \Delta b$, where $\bar{b}$ is the "exact" or specified component, and Δb depends on the random component Δx and changes in the external environment parameters (temperature, humidity, pressure, etc.). We will simplistically assume that Δx and $x_{\text{н}}^{\text{p}}$, as well as Δb and $\bar{b}$ are linearly independent, x and d are independent of each other, while d exists only at the design stage of the technological process, and Δx and $\Delta b -$ throughout the entire life cycle of the PSA unit. The regime (control) variables u also change significantly and affect the output coordinate y of the designed PSA unit.

For the convenience of further material presentation, we combine uncertain parameters $x_{\text{н}}^{\text{p}} + \Delta x$ and

$\bar{b} + \Delta b$ into a vector ξ and assume that ξ belongs to the specific region of uncertainty $\Xi = \{\xi_\rho \colon \xi_\rho^- \le \xi_\rho \le \xi_\rho^+\}$, $\rho = \overline{1, n_\xi}$ from the number space E^{n_ξ}. For fixed d, u и ξ, we can consider (1) - (16) as a system of differential and finite equations of the mathematical model for the dynamics of the gas mixture separation and purification technological process in order to determine y. Consequently, y is an implicit function of variables d, u and ξ: $y = y(d, u, \xi)$. The explicit form of this function, as a rule, is unknown, therefore, for each set of d, u, ξ, the output coordinates y of the technological process and the unit for gas mixture adsorption separation and purification are found by numerical solution of the system of dynamics equations (1) - (16) until the CSS process of the PSA unit operation is achieved (17) at $\tau = t_{\text{css}}$ [11, 12, 18-20, 23-29, 47].

The design parameters $d \in D$ of the PSA unit often include the number and type of adsorbers, the inner diameter D_{int} of the adsorber and the height L of the granular adsorbent bed [52, 58, 63, 79, 81, 82]. The regime (control) variables $u \in U$ of the unit operation include the duration of the adsorption τ_{ads} and desorption τ_{des} steps [5-7, 10-12, 18, 19, 24, 26, 28-31, 49, 52, 58, 63, 77-83], pressures P_{ads}, P_{des} at these steps [5-7, 10-12, 18, 19, 24, 26, 28-31, 49, 52, 58, 63, 77-83], the throughput of K_{v} valves [6 , 11, 12, 18, 19, 24, 77], the coefficient θ of the ratio of the gas mixture flows [31], enriched in the target gas and taken for the adsorbent regeneration, and the gas mixture at the inlet to the adsorber of the PSA unit. Using the opening degree of the valves ψ as control variables makes it possible to determine the optimal cyclogram of pressure changes at the adsorption-desorption steps [28, 29, 81].

When optimizing the operating regimes, the requirements of the technological regulations for the PSA unit operation must be met. When designing the technological process and the adsorption separation of gas mixtures, the design constraints (requirements of the technical design assignment) associated with ensuring the required quality of the products (purity of the concentrated gas), the set productivity of the unit, resource saving of the adsorbent, operational safety and environmental safety of production, etc. must be also satisfied [5-7, 10-12, 18, 19, 24, 26, 28-31, 49, 52, 58, 63, 77-83].

In a number of works, a restriction on the gas flow rate in the front adsorbent bed is applied [28-30, 81]. It is known that an increase in the gas flow rate in PSA processes inevitably leads to an increase in the aerodynamic resistance of the adsorbent bed, an increase in the abrasion of the adsorbent granules and a reduction in its service life [30]. This is due to the effect of the changing lateral von Karman forces on the granules, which cause oscillating displacements of the granules relative to each other. This effect is most likely manifested with a frequent change in the adsorption – desorption technological steps, when large pressure gradients appear in the adsorbent bed. The presence of dust in the product flow can lead to premature failure of expensive high-precision solenoid valves used for gas distribution inside the unit, which significantly increases the operation costs of the PSA units [30]. At the moment, the exact value of the critical flow rate providing resource saving of the adsorbent and high intensity of mass and heat transfer processes for different gas mixtures and adsorbents has not been established and is chosen by various authors in the range of ~ 0.08-0.25 m/s [28-30, 81].

In the formulations of optimization problems for the operation and design regimes (optimization of design parameters and regime variables) of gas mixture separation units according to the PSA method in the works cited above, the presence of uncertainty in the source data is not taken into account, and optimization problems are formulated in the form of a nonlinear programming task with constraints of equality/inequality type. In this case, the objective function and functions of constraints $g_j(u, d, y(t_{\text{css}})) = 0, j = 1,2, \dots, m$; $g_j(u, d, y(t_{\text{css}})) \le 0, j = m + 1, \dots, p$, which determine the sets of feasible solutions D, U, are twice continuous differentiable functions. These problem settings are known as Blackbox Optimization and Simultaneous Tailored Optimization [47, 84]. The difference between the Blackbox Optimization problem setting and Simultaneous Tailored Optimization is that in the Simultaneous Tailored Optimization setting, the condition for reaching the CSS regime (17) is included in the problem constraint $g_j(\cdot) \le 0$; due to this fact, the processor time is saved [47, 84].

In most of the works cited above, numerical methods of sequential unconstrained minimization (external and internal penalties, Lagrange multipliers), possible directions, and sequential quadratic programming are used to solve optimization problems [12]. The fact that the quadratic approximation (for example, used in Newton's method) gives good estimates of the unconditional minimum points is taken into account. Moreover, the group of quasi-Newtonian methods allows to take advantage of the quadratic approximation without explicit construction of a second-order approximating function at each iteration, which speeds up the computational process within the procedures for determining search directions, for example, for sequential optimization, reduced gradient and gradient design methods [58].

The sequential quadratic programming method is an adaptation of second-order methods to an optimization problem with constraints, while a procedure for the numerical solution of nonlinear Kuhn-Tucker equations is constructed instead of explicitly taking into account the constraints [47]. Each iteration of the classical Newtonian method for solving nonlinear Kuhn-Tucker equations is equivalent to solving some auxiliary optimization problem. Thus, sequential constrained quadratic minimization becomes sequential quadratic programming (SQP).

In particular, when solving optimizion problems of the operation regimes and design of air and synthesis gas separation units, the following methods are used: the SQP method [6, 11, 12, 31, 58, 77], the gOPT solver in the gPROMS software package [30, 49, 78], the IPOPT 3.4 solver in the AMPL software package [28, 29, 81]; the CVP SS solver [63], the Antigone solver in the GAMS software package [79]; the particle swarm method in the MatLab software package [64]; genetic algorithm II in the MatLab software package [26].

In [82], in order to solve optimizion problems of the operation regimes of the technological process for gas mixture separation and CO_2 extraction, the global optimization algorithm and the branch-and-bound method are used to reduce the search space (without using gradient methods). The proposed algorithm makes it possible to determine global extrema (minima) for 11 optimization problems from the above-cited works, and only two cases coincide with the solutions obtained in these papers by methods of finding a local extremum. Our studies have shown that good results when searching for a global extremum in the optimal design problem for PSA units for gas mixture separation are obtained when using the Direct Search method in the MatLab software environment; in 90% of practical problems, it is possible to find global extrema. The disadvantages of these methods in comparison with the SQP method are high computational costs.

In recent years, a number of articles devoted to solving problems of multicriteria optimization of PSA units have been published [36, 68, 69, 85, 86]. The need for setting the problem of multicriteria optimization is caused by the inconsistency of such technological parameters of the PSA process as the product gas purity, the degree of extraction and the productivity of the PSA unit [36, 68, 69, 85, 86]. In the formulations of multicriteria optimization problems, the corresponding combinations of these technical and economic indicators are considered as target functions. An approach based on an artificial neural network (ANN) is used to solve the problem. The neural network is trained using samples obtained from the verified model of the PSA process (1)-(16) using the Latin hypercube sampling strategy. In particular, in [85], the problem of multicriteria optimization of a nitrogen production unit with a purity of 99.5 vol. % and a recovery rate of 90% is solved using ANN; in [68], the problem of multicriteria optimization of the PSA unit for hydrogen extraction from a three-component gas mixture ($H_2/CO_2/CO=0.68/0.27/0.05$) on a CuBTC metal-organic framework adsorbent is solved using ANN; in [36], the problem of two-criterion optimization of a two-adsorber PSA unit for hydrogen extraction from a five-component gas mixture $H_2/CO_2/CH_4/CO/N_2$ = 38/50/1/1/10) is solved using ANN and the SQP algorithm; in [86], a design problem with two and three criteria for a four-adsorber PSA unit for hydrogen extraction with a purity of more than 99 vol.%. in the process of steam reforming of methane is solved using ANN and the genetic algorithm. The authors of [36, 68, 69, 85, 86] note a sufficiently high accuracy of the neural network's prediction of the PSA process behavior, while the time for solving the multicriteria optimization problem is reduced by an order of magnitude or more in comparison with the solution of this problem by traditional methods of penalty functions (methods of external and internal penalties), for example, from 15.7 h to 50 s [85].

Optimal design of gas mixture separation units by the PSA method in conditions of uncertainty

In the above-mentioned optimization problems of the operation regimes of the PSA units, the uncertainty of the source information is not taken into account: the uncertainty of the composition and temperature of the initial gas mixture, the inaccuracy of the experimental determination of the mathematical model coefficients (coefficients of mass and heat transfer, mass conductivity of the gas mixture components in the porous medium of the adsorbent), the change in the adsorbent characteristics from batch to batch during the PSA unit operation [41, 42]. Thus, for example, the component composition of synthesis gas obtained by the Lurgi method includes 38...40% H_2, 15...18% CO, 9...11% CH_4, 30...32% CO_2; the sizes of granules (particles) of industrial adsorbents, as a rule, are set by the range of the particle fraction sizes (for example, the line of granular zeolites 13X manufactured by Hong Kong Chemical Corp. has a particle size of 1.6 ... 2.5 mm, 3 ... 5 mm) [2]. In addition, the ambient temperature and pressure are randomly changed.

The presence of random parameters generates uncertainty in the source information which must be taken into account when setting and solving the optimization problem of designing a PSA unit [43-45]. In this case, the constraints in the formulation of optimization problems can be divided into two groups.

The first group include "hard" constraints which must be fulfilled despite the uncertainty ξ:

$$\max_{\xi\in\Xi} g_j(u,d,y(t_{\text{css}}),\xi) \le 0, j=\overline{1,p_1}. \quad (18)$$

It is advisable to refer the requirements for ensuring the purity of the extracted (concentrated) gas, resource conservation of the adsorbent, operational safety and environmental safety of production to this group of constraints [12, 28, 31, 49, 52, 58, 78, 83, 87, 88].

The second group includes softer constraints than in (18), which must be satisfied either on average or with a given confidence level P_{c}:

$$\Pr\{g_j(u,d,y(t_{\text{css}}),\xi) \le 0,\} \ge P_c\ , = \overline{p_2,p}\ , \quad (19)$$

where $P_{\text{c}} \in (0.85 \dots 0.95)$. This group of constraints should include the requirements for ensuring the specified unit productivity, the cost of production, etc. [6, 18].

The formulation of the optimal design problem under conditions of partial uncertainty consists in determining the design parameters d^* and the operating variables u^* of the cyclic unit for gas mixture adsorption separation and purification such that the average value $M_\xi\big(\varphi(u,d,y(t_{\text{css}}),\xi)\big)$ of the objective function (criterion) $\varphi(u,d,y(t_{\text{css}}),\xi)$ is achieved:

$$I(d^*,u^*) = \min_{d,u}\{M_\xi\big(\varphi(u,d,y(t_{\text{css}}),\xi)\big) \approx$$
$$\approx \textstyle\sum_{i\in J_1}\omega_j\,\varphi\big(u,d,y(t_{\text{css}}),\xi^i\big)\}, \quad (20)$$

and the unit operability is preserved (fulfillment of the design constraints (18), (19)) despite random changes in the vector ξ within the uncertainty region Ξ; where $M_\xi(\cdot)$ – symbol of the mathematical expectation; ω_i – weight coefficients of the quadrature formula approximating $M_\xi\big(\varphi(u,d,y(t_{\text{css}}),\xi)\big)$. The formulation of the design problem is primarily influenced by the level of the mathematical model accuracy which can be improved (or not) through the use of experimental information available during the operation of the gas mixture adsorption separation unit.

A characteristic feature of the one-step design problem for the PSA unit is the impossibility of specifying information regarding the uncertain parameters $\xi=\{\xi_\rho,\rho=\overline{1,n_\xi}\}$ during the unit operation. In this case, its design parameters $d\in D$ and operating variables $u\in U$ are equal since they do not change during the unit operation.

Let us show one of the possible and widely used in many works formulations of a one-step design problem for the PSA two-adsorber unit for gas mixture separation [47, 52, 84]: optimization criterion – the degree of product gas extraction (14); bonds – the mathematical model equations (1) - (16) of the dynamics of the technological process for gas mixture separation by the PSA method; constraints – by the purity of the product gas $\max_{\xi\in\Xi}\Big(\underline{c}^{\text{out}} - c^{\text{out}}(u,d,\xi,t_{\text{css}})\Big) \le 0$ in the gas mixture flow at the outlet of the PSA unit, the unit capacity $\max_{\xi\in\Xi}\Big(\underline{G}^{\text{out}} - G^{\text{out}}(u,d,\xi,t_{\text{css}})\Big) \le 0$, pressure drops $\Delta P_{\text{ads}}(t_{\text{css}})$, $\Delta P_{\text{des}}(t_{\text{css}})$ in the adsorbent bed ⟦ $\max_{\xi\in\Xi}\big(\Delta P_{\text{ads}}(t_{\text{css}}) - \overline{\Delta P}_{\text{ads}}(t_{\text{css}})\big) \le 0$, $\max_{\xi\in\Xi}\big(\Delta P_{\text{des}}(t_{\text{css}}) - \overline{\Delta P}_{\text{ads}}(t_{\text{css}})\big) \le 0$, velocity of the gas mixture ν_{g} in the front adsorbent bed $\max_{\xi\in\Xi}\big(\nu_{\text{cr}} - \nu(u,d,\xi,z=0)\big) \le 0$, the ratio of the length (height) $6 \le L/D_{\text{int}} \le 14$ of the adsorbent bed L to the adsorber inner diameter D_{int}, allowable ranges $[d^-,d^+]$, $[u^-,u^+]$ of design parameters $d^- \le d \le d^+$ and operating (control) variables $u^- \le u \le u^+$.

To solve the one-step design problem, the following iterative approach is often used, which makes it possible to reduce the original optimal design problem under conditions of interval uncertainty of the source data to solving a sequence of deterministic nonlinear programming tasks using a highly efficient sequential quadratic programming method [44].

It is possible to show one of the possible and frequently used algorithms for solving the one-step problem (18) - (20), (1) - (16) of designing a PSA unit with mixed constraints (18), (19) [44, 52]. A priori, the set $S_1=\{\xi^i\colon \xi^i\in\Xi, i\in J_1\}$ of approximation points and the set $S_2=\{\xi^l\colon \xi^l\in\Xi, l\in J_2\}$ of "critical" points are introduced, at which the constraints (18), (19) of a one-step optimization problem can be violated. Since the functions $g_j(\cdot), j=\overline{1,\mathrm{p}}$ are convex, it is expedient to include the corner points $\xi_\rho^-, \xi_\rho^+, \rho=\overline{1,n_\xi}$ of the uncertainty (polyhedron) domain $\Xi\subset E^{n_\xi}$ in the initial set of critical points $S_2^{(0)}$.

The algorithm for solving the one-step design problem consists of the following steps.

Step 1. Set the initial iteration number $k=1$, the set of approximation points $\xi^i, i\in J_1, \xi^i\in S_1$, the initial set of critical points $S_2^{(0)}=\{\xi^l\colon \xi^l\in\Xi\,, l\in J_2^{(k-1)}\}$, initial approximations of the design parameters $d^{(0)}$ and regime variables $u^{(0)}$.

Step 2. Find a solution to the auxiliary problem (A) using the method of sequential quadratic programming: it is required to determine vectors of design parameters $\hat{d}^{(k)}\in D$ and regime variables $\hat{u}^{(k)}\in U$ such that

$$I\big(\hat{d}^{(k)},\hat{u}^{(k)}\big) = \min_{d,u}\textstyle\sum_{j\in J_1}\omega_j\varphi\big(u,d,y(t_{\text{css}}),\xi^j\big) \quad \text{(A)}$$

with bonds (1) - (16) and constraints

$$g_j\big(u,d,y(t_{\text{css}}),\xi^i\big) \le 0,\ j=\overline{1,p_1}\,, \xi^i\in S_1, i\in J_1\ ;$$
$$g_j(u,d,y(t_{\text{css}}),\xi^l) \le 0, j=\overline{p_1,p_2}\,, \xi^l\in S_2^{(k-1)}, l\in J_2\ ,$$

and determine the values of the vectors $\hat{d}^{(k)}, \hat{u}^{(k)}$ and the objective function $I\left(\hat{d}^{(k)}, \hat{u}^{(k)}\right)$.

Step 3. Check the fulfillment of “stiff” constraints (18): solving p_1 of extreme problems: $\max\limits_{\xi \in \Xi} g_j\left(\hat{u}^{(k)}, \hat{d}^{(k)}, y(t_{\text{css}}), \xi\right), j = \overline{1, p_1}$, and determining p_1 of the points $\hat{\xi}^{(k),j}, j = \overline{1, p_1}$. Check the fulfillment of “soft” constraints (19) by the method of simulation modeling according to the uniform distribution law for uncertain parameters $\xi \in \Xi$ и $P_c = 0{,}9$: $\Pr\left\{g_j\left(u^{(k)}, d^{(k)}, y(t_{\text{css}}), \xi\right) \leq 0\right\} \geq \mathrm{P_c}, j = \overline{p_1, p_2}$ and determine the points $\check{\xi}^{(k),\lambda}$, where $\lambda \in \overline{p_2, p}$, at which the probabilistic constraints are violated, i.e. $\Pr\left\{g_j\left(u^{(k)}, d^{(k)}, y(t_{\text{css}}), \check{\xi}^{(k),\lambda}\right) \leq 0\right\} < P_c, j = \overline{p_2, p}$.

Step 4. Form the set of points $\xi^{(k)}$, at which constraints (18), (19) are violated:

$$R^{(k)} = \left\{ \begin{array}{l} \xi^{(k)}: g_j\left(u^{(k)}, d^{(k)}, y(t_{\text{css}}), \hat{\xi}^{(k),j}\right) > 0, j = \overline{1, p_1} \wedge \\ \Pr\left\{g_j\left(u^{(k)}, d^{(k)}, y(t_{\text{css}}), \check{\xi}^{(k),\lambda}\right) \leq 0\right\} < P_c, j = \overline{p_2, p} \end{array} \right\}.$$

If this set is empty, then the solution to the problem is obtained, i.e. $d^* = \hat{d}^{(k)}$, $u^* = \hat{u}^{(k)}$, $I(d^*, u^*) = I\left(\hat{d}^{(k)}, \hat{u}^{(k)}\right)$, and the algorithm ends its work; otherwise, one should go to step 5.

Step 5. Form a new set of critical points $S_2^{(k)} = S_2^{(k-1)} \cup R^{(k)}$, set $k := k + 1$, a set $d^{(k)} = \hat{d}^{(k-1)}$, $u^{(k)} = \hat{u}^{(k-1)}$ and go to step 2.

The above algorithm turned out to be quite effective in the optimal (according to the criteria of the extraction degree and profit from the oxygen production) design of PSA units for air oxygen enrichment with oxygen purity of 45 to 95.5 vol.% and a capacity of up to 4 nl/min [52, 89]. The disadvantage of this algorithm is an increase in the number of critical points at each iteration and, accordingly, the number of constraints taken into account.

More meaningful and economically profitable problem is the two-step design of the PSA process and unit [90]. The fundamental difference between the one-step and two-step problems is that in the two-step problem the roles of the variables d and u are different; so the variables d are still constant during the PSA unit operation, while the variables u can be changed and adjusted to fulfill the constraints (18), (19) of the optimization problem. In this case, one can face the need to clarify the uncertain parameters $\bar{\xi} = \{\bar{\xi}_\rho, \rho = \overline{1, n_\xi}$ during the PSA unit operation and solving the internal optimization problem: for fixed values of design d and refined uncertain $\bar{\xi} \in \Xi$ parameters, it is required to define the control vector $\hat{u}$ such that

$$\hat{\varphi}\left(d, \hat{u}, y, \bar{\xi}\right) = \min_{u \in U} \varphi\left(d, u, y, \bar{\xi}\right)$$

with bonds (1) - (16) and constraints (18) and/or (19).

In fact, the solution of the two-step optimization problem makes it possible to obtain the dependency $u^*(\xi)$, and when clarifying the uncertain parameters $\bar{\xi}$ during the PSA unit operation – the optimal value of the vector of regime variables $u^*(\bar{\xi})$ which is realized with the help of the automatic stabilization system.

Thus, two-step design makes it possible to determine a more economical equipment “structure” and a technological regime of the PSA unit operation in comparison with one-step design.

Since until present there is no complete theory and relatively simple (engineering) computational algorithms for determining the solution $u^*(\xi)$ of the two-step design problem, the following approach associated with the current control of the values of the uncertain parameters $\bar{\xi}$ during the PSA unit operation can be proposed. Next, it is necessary to determine the optimal value of the vector of regime variables $u^*(\bar{\xi})$ according to the solution of the two-step optimization problem. The implementation of the new regime $u^*(\bar{\xi})$ at the PSA unit is possible with the help of an automatic stabilization system.

CONCLUSION

As a result of the literature review in the field of mathematical modeling, optimization and design of technological processes for gas mixture adsorption separation, it has been found that, despite the rapidly increasing number of works in the field of cyclic adsorption processes and units for gas mixture separation and purification, the creation of industrial unit prototypes is constrained by the problems of insufficiently complete knowledge of the properties and regimes of their functioning, imperfection of the design of cyclic adsorption equipment from the standpoint of energy and resource saving, the methodology for creating and researching resource-saving cyclic adsorption processes and units for gas mixture separation and purification, algorithmic and information support for their optimal design in conditions of uncertainty of the source data.

A generalization of scientific achievements has been made and the following is recommended on its basis: 1) the methodology for research and creation of resource-saving cyclic adsorption processes and units for multicomponent gas mixture separation using the methods of chemical engineering processes and devices, system analysis, physical and mathematical modeling, optimization of regimes and design of PSA units in conditions of partial uncertainty of the source data; 2) the procedure and the heuristic algorithm for constructing a mathematical model of the multicomponent gas mixture separation and product gas extraction processes, including obtaining the mathematical model structure (or structural synthesis of the model), obtaining experimental data on the studied technological process on special laboratory facilities, parametric identification of the mathematical model using experimental data, analyzing and ensuring the adequacy of the mathematical model; 3) the structure of the model equations of all the technological scheme elements of the multi-adsorber PSA unit for separating and purifying gas systems as applied to hydrogen, oxygen and nitrogen extraction; 4) the method for calculating mass transfer and mass conductivity coefficients of the gas mixture components in the porous medium of the adsorbent; 5) the method of lines for solving the mathematical model equations of the dynamics of the technological process for gas mixture separation and product gas extraction by the PSA method using the solvers of Aspen Adsorption, Comsol Multiphysics, Ansys Fluent software products intended for solving problems of mathematical physics; 6) formulation of Blackbox Optimization and Simultaneous Tailored Optimization problems and effective methods of sequential quadratic programming (SQP) for optimizing the operation regimes and optimal design of technological processes and units for gas mixture adsorption separation and product gas extraction (hydrogen, oxygen and nitrogen) by the PSA method; 7) formulation of one- and two-step optimization problems in the design of PSA units under conditions of partial uncertainty of the source data and some heuristic approaches and computational algorithms for solving one-step optimization problems, which make it possible to determine the optimal values of design parameters and regime variables for the cyclic technological process equipment and the unit for gas mixture adsorption separation and purification, the optimality criterion and fulfillment of the requirements of the technical design specifications regardless of the values taken by uncertain parameters from the given intervals of their possible change.

The use of the latest advances in the design of PSA units makes it possible to implement a “high-speed” technological process of pressure swing adsorption while achieving a high degree of the product gas purity (for hydrogen – up to 99.99 vol.%, for oxygen – from 45 vol.% to 95 vol.% and higher, for nitrogen – up to 99.9995 vol.%); adjustable cycle speed; the minimum time to set the unit into the operation (cyclic steady state) regime; low consumption rates of the gas mixture per unit of product gas, which can significantly reduce the cost of electricity for compressor equipment; resource saving of the expensive adsorbent.

Based on the review results, the following promising directions in the field of mathematical modeling, optimization of operation regimes and design of PSA units, which can provide intensification and further development of cyclic processes of multicomponent gas mixture adsorption separation and improvement of equipment and technological design of PSA units, can be identified: 1) CFD-modeling which allows solving 2D and 3D-dimensional mathematical modeling problems of gas mixture separation processes in adsorbers with radial or spiral directions of the gas flow, taking into account the unevenness of its distribution in the porous medium of the adsorbent, stagnant zones and a decrease in the dynamic capacity of the adsorbent during the adsorption process of gas mixture separation in adsorbers with block adsorbents and granular adsorbents with complex granule shape; 2) multicriteria design of PSA units using the mathematical apparatus for training artificial neural networks which ensure high approximation accuracy of the mathematical model equations (1)-(16) and high speed of obtaining solutions to optimization problems of operation regimes and design of PSA units; 3) two-step design of PSA units, which allows to obtain more economical “structures” of units in comparison with one-step design and to correct the optimal values of operation variables according to refined uncertain parameters during the PSA unit operation; however, until present, there are no comparatively simple (engineering) computational algorithms for determining the dependencies of the vector of optimal regime variables on uncertain parameters at the design stage of the PSA unit.

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