Numerical study of cyclic adsorption processes of air oxygen enrichment in dynamics

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Abstract. The paper discusses the results of numerical analysis of the properties and modes of the adsorption air separation process and oxygen concentration with purity of ~90% carried out in a double-adsorber PSA unit with a 13X granular zeolite adsorbent with capacity of up to 2 l/min. Calculation experiments have been performed using the developed mathematical model and the influence of perturbations (temperature, composition and pressure of atmospheric air) on the dynamics of the process, the unit performance, the extraction degree and oxygen purity has been investigated. It has been established that the most effective control action is the pressure at the compressor outlet, the increase in which from 2 to 6×10⁵ Pa leads to the increase in the extraction degree and oxygen concentration on average by ~57% and ~12 vol.% respectively.

1. Introduction

Short-cycle processes of gas mixture adsorption separation are widely used in industry for hydrogen extraction, air oxygen enrichment, non-heated drying of gases, hydrocarbon separation, carbon dioxide concentration, methane extraction, etc. One of the actual tasks in the field of adsorption separation is air separation and oxygen concentration in medical oxygen concentrators [1–5].

When designing medical oxygen concentrators, it is necessary to take into account that the composition, temperature and pressure of atmospheric air can vary randomly in a certain range of possible values. In this case, the true values of these parameters are unknown, and they can take any values from the specified intervals. Therefore, the purpose of this work is a numerical study of the effect of perturbations (temperature, composition and pressure of atmospheric air) on the extraction degree, production oxygen purity and the pressure swing adsorption (PSA) unit capacity.

| Table 1. List of accepted symbols |
|-----------------------------------|
| $A_1, A_2$ – adsorbers           | $R$ – receiver                  |
| $a$ – concentration in the adsorbent, mol/m$^3$ | $S_{sp}$ – area of specific surface of adsorbent pores, m$^2$/m$^3$ |
| $a^*$ – equilibrium concentration, mol/m$^3$ | $T_a$ – adsorbent temperature, K |
| $C$ – compressor                 | $T$ – temperature, K            |
| $c_{pa}$ – specific heat capacity of adsorbent, J/(kg·K) | $t$ – time, s                   |
| $c_{pg}$ – specific heat capacity of gas mixture, J/(mole·K) | $t_{ads}$ – adsorption (half cycle) time, s |
| $D_A$ – internal diameter of the adsorber, m | $y$ – concentration, vol.%     |
2. Mathematical description of the oxygen enrichment process

The technological process of air separation and oxygen production is carried out in a double-adsorber PSA unit with a granular synthetic adsorbent 13X [6] (figure 1). The PSA unit (figure 1) is used for producing oxygen with purity of ~90-95 vol.% from atmospheric air containing: 1) oxygen in the amount of ~20.8 vol.%, nitrogen ~78.2 vol.%, argon and other impurities ~ 1 vol %. The initial gas-air mixture is supplied into the unit after preliminary drying with increased relative atmospheric pressure $P_{in}$. The pressure rise in the adsorbers is performed by opening the inlet valves $v_1$, $v_2$, through which the gas is supplied to the layer of the granular bulk.
adsorbent 13X. The oxygen-enriched air is removed from the adsorbers through the check valves \( v_{5}, v_{7} \) and sent to the consumer through the receiver \( R \). Countercurrent regeneration of the adsorbent in the adsorbers is carried out by means of the throttle \( v_{6} \), through which the oxygen-enriched air enters the adsorber for nitrogen desorption predominantly. The desorbed flow is discharged into the atmosphere through the exhaust valves \( v_{3}, v_{4} \).

The analysis of the PSA–air oxygen enrichment process allowed us to determine the control \( (t_{ads} = t_{x}/2, P^{in}, \theta, \Psi) \), perturbing \( (y_{env}, T_{env}, P_{env}) \), design \( (L, D_{A}, d_{g}, K_{g}, G_{c}) \) and output \( (y_{o}^{out}, Q, \eta) \) variables.

During \( O_{2}, N_{2} \) adsorption by zeolite adsorbents in the adsorbers of the PSA unit, the following mass and heat exchange processes take place: a) \( O_{2}, N_{2} \) diffusion in the gas-air mixture flow; b) \( O_{2}, N_{2} \) mass transfer and heat exchange between the gas phase and the adsorbent; c) \( N_{2} \) adsorption predominantly on the surface and in the micropores of the zeolite adsorbent granules with the release of heat and \( N_{2} \) desorption from the micropores and from the surface of the granules with the heat absorption. The analysis of physical modeling of these processes showed that \( O_{2}, N_{2} \) diffusion and the heat transfer in the gas and solid phases are carried out mainly in the axial direction relative to the gas mixture flow in the adsorber (i.e. along the height of the adsorbent). At the same time, the process of air oxygen enrichment during \( N_{2} \) adsorption takes place in the outer-diffusion area and is determined by the external mass transfer coefficient, as well as by equilibrium ratios of \( O_{2} \) and \( N_{2} \) concentrations in the phases.

In the mathematical description of the air oxygen enrichment process in the PSA unit, the following assumptions were made: 1) the atmospheric air is a three-component gas-air mixture (contains \( 1 - O_{2} \) with a concentration of 20.8 vol.\%, 2 – \( N_{2} \) with a concentration of 78.2 vol.\%, 3 – \( Ar \) and other impurities with a concentration of 1.0 vol.\%) \([7-9] \) and is considered as an ideal gas, which is quite acceptable when the pressure in the adsorber is up to \( 200 \cdot 10^{5} \) Pa \([10]\); moreover, the concentration of argon and other impurities in the gas-air mixture does not change with the air oxygen enrichment; 2) the geometrical dimensions of the adsorption layer are constant for a given lifetime of \( \sim 10^{3} \) h \([11]\); 3) the adsorbent layer is a continuous environment with porosity \( \varepsilon \approx 0.394 \) \([12]\); 4) the adsorption equilibrium (adsorption isotherm) is described by the Dubinin–Radushkevich equation \([13]\); 5) the desorption branches of \( O_{2}, N_{2} \) adsorption isotherms on zeolite 13X coincide with the adsorption branches \([14]\); 6) the air temperature in the receiver is equal to the air temperature at the adsorber outlet, the heat loss to the environment is negligible.

In accordance with accepted assumptions, the mathematical description of the air separation process includes the following equations:

Component-wise material balance of the components \( (O_{2}, N_{2}) \) in the gas phase flow, taking into account the longitudinal mixing in the adsorbent layer

\[
\frac{\partial y_{k}(x, t)}{\partial t} + \frac{(1 - \varepsilon)}{\varepsilon} \frac{\partial a_{k}(x, t)}{\partial t} + v_{g} \frac{\partial y_{k}(x, t)}{\partial x} = \frac{\partial}{\partial x} \left( D_{g}(x) \frac{\partial y_{k}(x, t)}{\partial x} \right), \quad k = 1, 2
\]  

Adsoption–desorption kinetics

\[
\frac{\partial a_{k}(x, t)}{\partial t} = \beta_{k} S_{sp}(a_{k}^{*} - a_{k}(x, t))
\]  

Heat transfer in the gas and solid phases, taking into account the convective component and heat conductivity

\[
c_{pg} \frac{\partial T_{g}(x, t)}{\partial t} + c_{pg} v_{g} \frac{\partial T_{g}(x, t)}{\partial x} = \frac{\alpha}{\varepsilon} S_{sp}(T_{g}(x, t) - T_{w}(x, t)) = \lambda_{g} \frac{\partial^{2} T_{g}(x, t)}{\partial x^{2}}
\]

\[
c_{ps} \frac{\partial T_{s}(x, t)}{\partial t} + \alpha S_{sp}(T_{s}(x, t) - T_{w}(x, t)) = \sum_{k} \frac{\partial a_{k}(x, t)}{\partial t} = \lambda_{s} \frac{\partial^{2} T_{s}(x, t)}{\partial x^{2}}
\]

Changes in the gas mixture flow rate and gas mixture pressure along the height of the adsorbent:
\[ \sum_{j} \frac{\partial v_j}{\partial x} - \frac{\partial}{\partial x} \left( \sum_{k} y_k \right) = 0 \] (5)

\[ \frac{\partial P}{\partial x} = \left( \frac{150(1-\epsilon)^2}{(g^2\epsilon)^2} e^{-\mu_{y_y} v_{y_y}} + 1.75M_{y_y} \rho_{y_y} (1-\epsilon) \right) \frac{v_{y_y}^2}{d_{y_y}^2\epsilon^2} \] (6)

The values and formulas for calculating the coefficients and constants of the model (1)–(6) are given in [15]. The boundary and initial conditions for the model equations (1)–(6) are similar to those given in [15]. The solution of the model (1)–(6) equations was carried out by the method of lines (pdepe) in the MatLab software environment.

Checking the adequacy of the mathematical model was carried out according to the results of independent experiments, i.e. different from the experimental data used to identify the model. The mismatch between the calculated by the model and experimental data was estimated by the formula:

\[ \delta_{\text{max}} = \max_{j=1,n} \left[ \frac{y_{1,j}^{\text{out}, e} - y_{1,j}^{\text{out}, \text{model}}(t_{\text{ads}, j})}{y_{1,j}^{\text{out}, e}} \right] \]

Figure 2. The experimental and calculated by the model dependences of production oxygen concentration: a) for different half-cycle time \( t_{\text{ads}} \); b) along the height of the adsorbent layer at \( t_{\text{ads}} = 5s \) (\( \Delta \) – experiment, \( \text{—} \) calculation by the model).

The maximum relative error \( \delta_{\text{max}} \) in the mismatch between the calculated \( y_{1,j}^{\text{out}, e} \) and experimental data \( y_{1,j}^{\text{out}, e} \) does not exceed 10.5% (figure 2), which allows to use the mathematical model for technological calculation purposes and optimizing the air oxygen enrichment process by the PSA method with acceptable practical accuracy.

3. Results and discussions

In the article [15] it was studied the effect of control variables on output variables: in order to study the effect of perturbations (temperature, composition and pressure of atmospheric air) on the extraction degree, oxygen purity and the PSA unit capacity, the numerical analysis was performed. Variables and ranges of their changes are presented in Table 2.

| Names of variables | Nominal values | The range of changes |
|--------------------|----------------|---------------------|
| \( t_{\text{ads}}, s \) | 5              | 0.5–20              |
| \( p^{\text{in}}, 10^5 \text{ Pa} \) | 4              | 2–6                |
| \( \theta \) | 1.7            | –                   |

| Names of variables | Nominal values | The range of changes |
|--------------------|----------------|---------------------|
| \( L, \text{ m} \) | 0.2            | –                   |
| \( D_{A}, \text{ m} \) | 0.04           | –                   |
| \( K_{v}, \text{ l/min} \) | 15             | –                   |

Table 2. The source data for calculation experiments
A series of calculation experiments was carried out to study the dynamics of the PSA–air oxygen enrichment process in a double-adsorber PSA unit: the effect of half-cycle time $t_{ads}$, pressure $P^{in}$, temperature $T^{in}$ and composition $y^{in}$ of the gas-air mixture at the compressor outlet on the extraction degree $\eta$, production oxygen concentration $y^{out}$ and the unit performance $Q$.

The dynamics of the air pressure $P$ in the adsorber at the adsorption and desorption stages at various values of half-cycle time $t_{ads}$ is presented in figure 3a. The analysis of the graphs shows that at half-cycle time values $t_{ads} = 1$ s and $t_{ads} = 5$ s, the current pressure $P$ in the adsorbers cannot reach $P^{in}$ at $t_{ads} = 20$ s the pressure $P=P^{in}$ is reached after 10 s (curves 1, 2).

The graphs of nitrogen concentration $a_2$ in the adsorbent at the height of the layer $L$ at various values of half-cycle time $t_{ads}$ (figure 3b) show that as the time of the adsorption stage $t_{ads}$ increases from 1 to 20 s and, accordingly, the pressure at the adsorption stage (figure 3a), the attainable value of nitrogen concentration $a_2$ in the front adsorbent layer (at the point $L=0$) increases from 310 to 440 mol/m$^3$. This is explained by the increase in the equilibrium nitrogen concentration $a^*$ in the adsorbent when the pressure in the adsorber increases [13]. At $t_{ads} = 20$ s the adsorption capacity is exhausted in the layer up to 0.05 m long (figure 3b, curve 3). Despite the partial filling of the adsorption capacity in the layer in the area from 0.05 to 0.2 m and the possibility of further nitrogen adsorption, the beginning breakthrough of a part of the gas-air flow (figure 3b, curve 3, $L=0.2$ m) and the need to ensure concentration at the unit outlet of 90 vol.% do not allow to increase $t_{ads}$ above 20 s.

The analysis of dependences in figures 4–6 shows that each pressure value at the compressor outlet $P^{in}$ (figure 4a), temperature $T_{env}$ (figure 5a, curves 1–3 and figure 5b, curves 1–3) and environment
pressure $P_{\text{env}}$ (figure 6a, curves 1–3 and figure 6b, curves 1–3) has a value of the adsorption stage time $t_{\text{ads}}$ at which the maximum concentration value $y_{\text{out}}^1$ is reached (for example, for $P_{\text{in}}=2\cdot10^5$ Pa, $y_{\text{out}}^1=80$ vol.\% at $t_{\text{ads}}=5$ s (figure 4a, curve 1)). When the adsorption stage time is less than 5 s, the adsorbent is not sufficiently regenerated (for example, for $P_{\text{in}}=2\cdot10^5$ Pa at a time interval $t_{\text{ads}}$ from 0.5 to 5 s (figure 4a, curve 1), and when the time is longer, the production oxygen concentration $y_{\text{out}}^1$ decreases due to the breakthrough of the gas-air flow parts without nitrogen adsorption (for example, for $P_{\text{in}}=2\cdot10^5$ Pa at a time interval $t_{\text{ads}}$ from 5 to 20 s (figure 4a, curve 1)), which leads to the decrease in the efficiency of the PSA unit.

It should be noted that the increase in the pressure at the compressor outlet $P_{\text{in}}$ from $2\cdot10^5$ to $6\cdot10^5$ Pa leads to the decrease in the adsorption stage time $t_{\text{ads}}$ from 5 to 2 s (figure 4a, curves 1, 3), the increase in the value $y_{\text{out}}^1$ from 80 to 92.3 vol.\%, and the increase in the extraction degree $\eta$ from 11.9\% to 69.5\% (figure 4b, curves 1, 3) and the unit capacity $Q$ for pure oxygen from 0.25 to 4.9 l/min (figure 4b, curves 4, 6).

![Figure 4](image_url)  
**Figure 4.** The dependence of production oxygen concentration $y_{\text{out}}^1$ (a), extraction degree $\eta$ and the unit capacity $Q$ for pure oxygen (b) on half-cycle time $t_{\text{ads}}$ at the pressure in the compressor outlet:
1, 4–$P_{\text{in}}=2\cdot10^5$ Pa; 2, 5–$P_{\text{in}}=4\cdot10^5$ Pa; 3, 6–$P_{\text{in}}=6\cdot10^5$ Pa.

![Figure 5](image_url)  
**Figure 5.** The dependence of production oxygen concentration $y_{\text{out}}^1$ (a) and air flow rate at the unit outlet $G_{\text{out}}$ on half-cycle time $t_{\text{ads}}$ at the compressor outlet pressure $P_{\text{in}}=4\cdot10^5$ Pa (a), $P_{\text{in}}=6\cdot10^5$ Pa (b) and environment temperature: 1, 4–$T_{\text{env}}=243$ K; 2, 5–$T_{\text{env}}=293$ K; 3, 6–$T_{\text{env}}=303$ K.
The extraction degree $\eta$ with increasing half cycle time $t_{ads}$ raises when reaching the plateau (figure 4b, curves 1–3; figure 6a, curves 4–6; figure 6b, curves 4–6). This effect is explained by the fact that increasing the pressure in the adsorber leads to decreasing the fraction of the flow taken for desorption through the throttling device $v_6$.

The graphs in figure 5 demonstrate that the increase in the environment temperature $T_{env}$ by 10 K (from 293 K to 303 K) leads to the decrease in the oxygen concentration $y_1^{out}$ by an average of ~5 vol.% (figure 5a, curves 1–3 and figure 5b, curves 1–3), since the value of nitrogen equilibrium concentration $a^*$ in the adsorbent decreases. At the same time the flow rate $G^{out}$ increases (figure 5a, curves 4–6 and figure 5b, curves 4–6), because due to the breakthrough of a part of the gas-air flow (without nitrogen adsorption) the unit starts operating in the filtration mode. The dependences of the extraction degree $\eta$ and the unit capacity $Q$ for pure oxygen on half cycle time $t_{ads}$ are the same for different values of the environment temperature $T_{env}$ (not shown in the figures). At temperatures $T_{env}$ above 293 K, the increase in the pressure $P^{in}$ at the compressor outlet from $4\cdot10^5$ to $6\cdot10^5$ Pa allows to increase the oxygen concentration value on average by ~4 vol.% (figure 5a, curve 3 and figure 5b, curve 3).

The dependency in figure 6a shows that the decrease in oxygen concentration $y_1^{in}$ in the initial gas-air mixture by 1 vol.% (from 20.8 vol.% – figure 4a, curves 1–3, to 19.8 vol.% – figure 6a, curves 1–3) leads to the decrease in production oxygen concentration $y_1^{out}$ at the unit outlet by ~4 vol., while the extraction degree $\eta$ does not change (figure 6a, curves 4–6 and figure 4a, curves 4–6). Increasing the pressure $P^{in}$ at the compressor outlet from $4\cdot10^5$ to $6\cdot10^5$ Pa leads to the increase in production oxygen concentration $y_1^{out}$ by ~2.5% vol. (figure 6a, curves 2–3), while the extraction degree $\eta$ increases by ~15% (figure 6a, curves 5–6).

The analysis of dependences in figure 6b reveals that the decrease in the environment pressure $P_{env}$ from $1\cdot10^5$ to $0.25\cdot10^5$ Pa (at the increase in the height of the unit location) leads to the increase in production oxygen concentration $y_1^{out}$ by ~2 vol.% (figure 6b, curves 1, 3) and the extraction degree...
η – by ~20 vol.% (figure 6b, curves 4, 6). It is explained by the fact that the decrease in the environment pressure and the constant pressure at the compressor outlet \(P^{\text{in}}\) results in the increase in the pressure ratio coefficient at the adsorption and desorption stages [15].

4. Conclusion
During the calculation experiments, it has been found that the effect of perturbations (temperature, composition and pressure of atmospheric air) has a significant impact on the extraction degree, oxygen purity and the unit capacity: 1) the increase in environment temperature \(T_{\text{env}}\) by 10 K (from 293 K to 303 K) leads to the decrease in oxygen concentration \(y^{\text{out}}_1\) on average by ~5 vol.%; 2) the decrease in oxygen concentration \(y^{\text{in}}_1\) in the initial gas-air mixture by 1 vol.% (from 20.8 vol.% to 19.8 vol.%) results in the decrease in oxygen concentration \(y^{\text{out}}_1\) at the unit outlet by ~4 vol.%; 3) the decrease in the environment pressure \(P_{\text{env}}\) from 1·10\(^5\) to 0.25·10\(^5\) Pa leads to the increase in production oxygen concentration \(y^{\text{out}}_1\) by ~2 vol.% and the extraction degree \(\eta\) by ~20 vol.%. One of the most effective control actions is pressure \(P^{\text{in}}\) at the compressor outlet: 1) the increase in pressure \(P^{\text{in}}\) from 2·10\(^5\) to 6·10\(^5\) Pa leads to the increase in oxygen purity \(y^{\text{out}}_1\) from 80 to 92.3 vol.%, as well as to the increase in the extraction degree \(\eta\) from 11.9% to 69.5 % and the unit capacity \(Q\) for pure oxygen from 0.25 to 4.9 l/min; 2) at temperature \(T_{\text{env}} = 303\) K, the increase in pressure \(P^{\text{in}}\) from 4·10\(^5\) to 6·10\(^5\) Pa allows to raise the value of oxygen concentration \(y^{\text{out}}_1\) on average by ~4 vol.%; 3) when the oxygen concentration \(y^{\text{in}}_1\) in the initial gas-air mixture decreases by 1 vol.% (from 20.8 vol.% to 19.8 vol.%), the increase in pressure \(P^{\text{in}}\) from 4·10\(^5\) to 6·10\(^5\) Pa leads to the increase in the extraction degree by ~15% and oxygen purity by ~2.5 vol. %.

The research allowed to obtain new scientific results which can be used with high efficiency: 1) in formulating and solving optimization problems of cyclic modes of atmospheric air adsorption separation processes in order to concentrate oxygen with purity of 90 ... 95 vol.%; 2) in the optimal design of new automated processes and PSA units with cyclically varying pressure for separating and purifying multicomponent gas mixtures; 3) in the optimal design of small-sized medical oxygen concentrators and onboard oxygen-producing facilities of a new generation.

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