Mathematical modelling of cyclic pressure swing adsorption processes

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Abstract. The paper discusses the results of a numerical analysis of the properties and regimes of the adsorption air separation and oxygen concentration process with a purity of ~ 40-60%, carried out in a 2-adsorption vacuum-pressure plant with a granular zeolite adsorbent 13X with a productivity of $1.6 \times 10^{-5}$ m$^3$/s. Computational experiments were carried out using the developed mathematical model and the influence of temperature, pressure, reflux ratio, the duration of the adsorption and desorption stages, the harmonic fluctuations of the inlet pressure during the adsorption stage and the outlet pressure during the desorption stage on the kinetics, and the efficiency of the air separation process by the PSA method were investigated. It is established that the specially organized harmonic fluctuations of the inlet pressure at the stage of adsorption and outlet pressure during the desorption stage lead to an increase in the purity of product oxygen by 4% (vol.).

1. Introduction
The processes of pressure swing adsorption (PSA) are widely implemented in various fields: in chemical, petrochemical, food industry, medicine, pharmaceuticals, energy, aviation, and are intended for separation of multicomponent gas mixtures and concentration of target products in them. One of the relevant tasks in the field of adsorption separation of multicomponent gas mixtures is air separation and oxygen concentration with oxygen purity of ~ 40-60% in the product stream in PSA units with a capacity of $1.2 \times 10^{-5}$ m$^3$/s to $17 \times 10^{-5}$ m$^3$/s [1, 2].

The aim of this work was to analyze the effect of regime variables, design parameters and specially organized harmonic fluctuations of the inlet pressure during the adsorption stage and the outlet pressure in the desorption stage on the efficiency of the PSA process of air separation and oxygen concentration.

| Table 1. Symbols and abbreviations |
|-----------------------------------|
| $A_1, A_2$ – adsorbers            |
| $P_{\text{out}}^\text{ads}, P_{\text{out}}^\text{des}$ – pressure at the outlet of the unit at adsorption and desorption stages, $\times 10^5$ Pa |
| $a_i$ – sorption capacity of $i$ component of adsorbent, mole/m$^3$ |
| $b$ – exponent of the Langmuir-Freundlich equation |
| $C$ – compressor, $VC$ – vacuum pump |
| $R$ – receiver |
| $S$ – cross-sectional area of the adsorber, m$^2$ |
| $S_{\text{sp}}$ – specific surface area of adsorbent particles, m$^2$/m$^3$ |
\( D_g \) – diffusion coefficient of nitrogen and oxygen in gas-air flow, m\(^2\)/s

\( c_{ads,i}^{in} \) – concentration of i component of the gas-air mixture at the inlet during adsorption stage, mole/m\(^3\)

\( c_{ads,i}^{out}, c_{des,i}^{out} \) – concentration of the i component of the gas-air mixture at the outlet during adsorption stage, mole/m\(^3\)

\( c_{pg} \) – specific heat of gas-air mixture, J/(mole·K)

\( c_p \) – specific heat capacity of adsorbent, J/(mole·K)

\( c_{pc} \) – specific heat capacity of adsorbate, J/(mole·K)

\( D \) – diameter of adsorber, m

\( d \) – diameter of adsorbent granules, m

\( Env \) – external environment

\( G_{ads}^{in} \) – consumption of the gas-air mixture at the inlet during adsorption stage, m\(^3\)/s

\( G_{ads}, G_{des} \) – consumption of the gas-air mixture at the outlet during the adsorption and desorption stages, m\(^3\)/s

\( H \) – length (height) of adsorber, m

\( h_i \) – sorption heat of the i component of the mixture, J/mole

\( i = 1,2,3: 1 \) – oxygen, 2 – nitrogen, 3 – argon

\( k \) – adiabatic index of a gas mixture

\( k_p = P_{ads}/P_{des} \) – pressure ratio coefficient at adsorption and desorption stages

\( M_{g,i} \) – molar mass of the i component, kg/mole

\( P_{ads}^{in} \) – pressure at the inlet during adsorption stage, \( \times 10^5 \) Pa

\( T_a \) – adsorbent temperature, °C

\( T_{ads}^{in}, T_{des}^{out} \) – temperature of the gas-air mixture at the inlet during adsorption, °C

\( T_{ads}, T_{des} \) – temperature of the gas-air mixture at the outlet during adsorption and desorption stages, °C

\( T_{env} \) – environment temperature, °C

\( t \) – time, s

\( t_{ads} \) – duration of adsorption stage, s

\( t_{des} \) – duration of desorption stage, s

\( v_1, v_2, v_3, v_4, v_5, v_6, v_7, v_8 \) – isolator valves

\( W_i \) – mass flow of the gas-air mixture through the i valve, kg/s

\( x \) – spatial coordinate of the adsorption layer (height in the adsorber), m

\( \alpha \) – heat transfer coefficient from the solid phase (of the adsorbent) to the gas-air mixture, Wt/(K·m\(^2\))

\( \beta_1 \) – total mass transfer coefficient as referred to the concentration of adsorbate, 1/s

\( \lambda_g \) – coefficient of thermal conductivity of the mixture, Wt/(m·K)

\( \mu_g \) – dynamic viscosity of a gas mixture, H·s/m\(^2\)

\( \theta \) – reflux ratio, \( \theta = G_{des}/G_{ads} \)

\( \rho_a \) – adsorbent density, kg/m\(^3\)

\( \rho_g \) – gas-air mixture density, mole/m\(^3\)

\( \varsigma \) – sphericity coefficient of adsorbent granules

\( w \) – velocity of gas-air mixture, m/s

\( n \) – the number of fluctuations in the inlet pressure during adsorption stage

2. Materials and methods

The process of separation of air into oxygen and nitrogen is carried out by the PSA method using up-to-date technical equipment (2-adsorber \( A_1, A_2 \) vacuum pump PSA unit [3] with granular zeolite adsorbent \( 13X \) [4], compressor C, vacuum pump VC, adsorbers A, receiver R, and high-precision valves \( v_1, v_8 \), which are switched using the control unit) (Fig. 1).
Figure 1. Principal flow chart of oxygen concentration process

Analysis of the PSA process of air oxygen enrichment made it possible to determine input \((c_{ads}^{in}, G_{ads}^{in}, T_{ads}^{in})\); output \((c_{ads}^{out}, c_{des}^{out}, G_{ads}^{out}, G_{des}^{out}, P_{ads}^{out}, P_{des}^{out}, T_{ads}^{out}, T_{des}^{out})\); regime \((P_{ads}^{in}, k_{p} = P_{ads}^{in} / P_{des}^{in}, t_{ads}, t_{des}^{ads}, t_{des}^{des}, \gamma = t_{des} / t_{ads}, \theta)\); structural \((D, H, d)\) and disturbance \((T_{env})\) variables.

The mathematical model of the processes taking place in PSA adsorbers for air separation includes equations (1) - (5), which are presented in Table 2 and are described in [5-10].

| No. | Equation |
|-----|----------|
| (1) | The equation of the component material balance in the gas-air mixture flow along the height of the adsorbent layer:  
\[
\frac{\partial (wc_{i})}{\partial t} + \frac{\partial c_{i}}{\partial t} + \rho \frac{\partial a_{i}}{\partial t} = 0
\] |
| (2) | The equation of adsorption kinetics describing the mass transfer of adsorbate from a gas-air mixture to an adsorbent:  
\[
\frac{\partial a_{i}}{\partial t} = \beta_{i} (a_{i}^{*} - a_{i}) = 0, i = 1, n
\] |
| (3) | An equation describing the propagation of heat in a gas-air mixture along the height of an adsorbent:  
\[
c_{pg} \rho_{g} \frac{\partial T}{\partial t} + \varepsilon c_{pg} \rho_{g} \frac{\partial T}{\partial t} + P \frac{\partial T}{\partial t} - \frac{\partial w}{\partial t} a_{i}^{*} \frac{\partial^{2} T}{\partial x^{2}} + \alpha S_{sp} (T - T_{g}) = 0
\] |
| (4) | An equation describing temperature variation in an adsorbent:  
\[
\rho \left( c_{pg} + \sum_{i=1}^{n} (c_{pg} a_{i}) \right) \frac{\partial T_{a}}{\partial t} + \rho \sum_{i=1}^{n} \left( h_{i} \frac{\partial a_{i}}{\partial t} - \lambda_{a} \frac{\partial^{2} T_{a}}{\partial x^{2}} - \alpha S_{sp} (T - T_{g}) = 0
\] |
| (5) | The equation of conservation of momentum, which describes the pressure drop in the adsorbent:  
\[
\frac{\partial}{\partial t} \left( \sum_{i=1}^{n} (c_{pg} a_{i}) \right) + \frac{\partial P}{\partial t} + \rho \sum_{i=1}^{n} \left( h_{i} \frac{\partial a_{i}}{\partial t} - \lambda_{a} \frac{\partial^{2} T_{a}}{\partial x^{2}} - \alpha S_{sp} (T - T_{g}) = 0
\] |
layer:
\[
\frac{\partial (\rho, T)}{\partial x} = -150 \frac{(1-e)^2}{R \cdot (d\xi)^2} e^\frac{1-\epsilon}{\rho} w - 1.75 \sum_{i=1}^{n} c_i M_{g,i} \frac{(1-e)}{R \cdot d \xi e^w} w^2
\]

(6) The equilibrium concentration \( a^* \) is calculated from the Langmuir-Freundlich equation [11]:
\[
a^*_i = \frac{b_{p,i} \cdot c_i \cdot P \cdot 0.0224 e^{\frac{b_{p,i}}{T_a}}}{1 + \sum_{j=1}^{n} b_{p,j} \cdot c_j \cdot P \cdot 0.0224 e^{\frac{b_{p,j}}{T_a}}} + \frac{b_{s,i} \cdot c_i \cdot P \cdot 0.0224 e^{\frac{b_{s,i}}{T_a}}}{1 + \sum_{j=1}^{n} b_{s,j} \cdot c_j \cdot P \cdot 0.0224 e^{\frac{b_{s,j}}{T_a}}}, \quad i, j = 1, n.
\]

(7) The molar flow rate of the gas mixture through the \( i \) valve is calculated by formulas:
\[
G_i = \frac{W_i}{\sum_{j=1}^{n} c_i^n M_{g,j}} = K_i S_i P_i^n \sqrt{\frac{k \cdot \sum_{j=1}^{n} c_j^n M_{g,j}}{R \cdot T_i} \left(\frac{2}{k+1}\right)^{-\frac{k+1}{2(k-1)}}}
\]

A detailed description of the mathematical model (1) - (5), which is a system of nonlinear partial differential equations of parabolic type with initial and corresponding boundary conditions, is given in [5]. The solution of the model equations was carried out by the method of lines in the Matlab software environment [12]. The initial data for the computational experiment are presented in Table 3.

| Table 3. Initial data for the computational experiment |
|---------------------------------------------|
| Variables | Nominal values of variables | Varying range |
| \( t_{ads}, \text{s} \) | 40 | 10–90 |
| \( t_{des}, \text{s} \) | 40 | 10–90 |
| \( \gamma = t_{des} / t_{ads}, \text{s/s} \) | 1 | – |
| \( c_{1}^m, c_{2}^m, c_{3}^m, \% (\text{vol.}) \) | 20.8; 78.2; 1 | – |
| \( P_{ads}^m, \times 10^5 \text{ Pa} \) | 2.7 | 2.2; 2.7; 3.7; 5.2 |
| \( P_{des}^m, \times 10^5 \text{ Pa} \) | 0.75 | 0.25; 0.5; 0.75; 1 |
| \( k_p = P_{ads}^m / P_{des}^m \) | 3.6 | 2.7; 2.9; 3.6; 4.9; 5.4; 6.9; 10.8 |
| \( \theta, \text{m}^3/\text{m}^3 \) | 2 | 1.6; 1.8; 2; 2.2 |
| \( T_g, ^\circ \text{C} \) | 25 | 0; 25; 50 |
| \( T_{env}, ^\circ \text{C} \) | 25 | 0; 25; 50 |
| \( H, \text{m} \) | 0.5 | – |
| \( D, \text{m} \) | 0.05 | – |
| \( b_1, b_2, b_3, b_4, b_5, b_6, b_7 \) | 2.99\cdot10^3; 8.32\cdot10^5; 2152; 4\cdot10^5; 2.12\cdot10^6; 2098 | – |
| \( d, \times 10^{-3} \text{ m} \) | 0.5 | – |

The results of the computational experiment are presented in Fig. 2-4. The analysis of the dependence of the oxygen concentration at the outlet of the PSA unit on the duration of the adsorption stage (Fig. 2) allows one to conclude that for each value of reflux ratio \( \theta \) (Fig. 2a) and adsorption pressure \( P_{ads}^m \) (Fig. 2b), there is such duration of adsorption stage \( \tilde{t}_{ads} \) that the maximum concentration of product oxygen \( c_{out}^m \) is reached. At a shorter duration of adsorption stage \( t < \tilde{t}_{ads} \) (Fig. 2a), sufficient regeneration of the adsorbent is not ensured (for example, for \( \theta = 2.2 \) in the range...
from 7 to 27 s), and for a longer duration \( t > \tilde{t}_{\text{ads}} \), the oxygen concentration at the plant outlet decreases, as a result of exhausting the adsorption capacity of the adsorbent (for example, for \( \theta = 2.2 \) in the range from 27 to 90 s), which leads to a decrease in the efficiency of the PSA unit. It should be noted that an increase of \( \theta \sim 1.4 \) times (from 1.6 to 2.2) leads to an increase in the duration of adsorption stage \( t_{\text{ads}} \) by 2.3 times (from 27 s to 62 s) and the maximum concentration of product oxygen is reached. The increase in the adsorption pressure from 2.2 to \( 5.2 \times 10^5 \) Pa leads to an increase in the consumption rate from \( 8.34 \cdot 10^{-5} \) m\(^3\)/s to \( 16.67 \cdot 10^{-5} \) m\(^3\)/s, as well as to a decrease (from 64 s to 30 s) in the duration of adsorption stage when the maximum concentration of product oxygen is reached. In addition, with an increase in the adsorption pressure from 2.2 to \( 5.2 \times 10^5 \) Pa, the maximum oxygen concentration at the unit outlet is increased by 4% (from 43 to 47% (vol.)) due to an increase in the equilibrium nitrogen concentration in the adsorption stage \( a_{2,\text{ads}} \) (Equation 6).

From the analysis of the dependence of the oxygen concentration at the PSA unit outlet from the duration of the adsorption stage in Fig. 3a, it can be concluded that a decrease in the desorption pressure from \( 1 \times 10^5 \) to \( 0.25 \times 10^5 \) Pa and the duration of the adsorption and desorption stages from 35 s to 23 s leads to an increase in the maximum oxygen concentration in the product flow from 46 to 66% (vol.). This is explained by the fact that a decrease in the desorption pressure leads to an increase in the ratio of the pressures of adsorption and desorption and, correspondingly, to a decrease in the equilibrium concentration at desorption stage \( a_{2,\text{des}} \) (Equation 6).

Due to insufficient volume of the compressor’s receiver or its absence in the PSA unit, pressure fluctuations may occur. From the analysis of the graphs in Fig. 3b it follows that the presence of fluctuations in pressure \( P_{\text{out}} \) or \( P_{\text{ads}} \) (\( \tau = 3; \tau = 6 \)) allows one to increase concentration \( c_{\text{out},1}^{\text{ads}} \) by 1-4% (in comparison with \( c_{\text{out},1}^{\text{ads}} \) in the absence of fluctuations, \( \tau = 0 \)). The presence of \( P_{\text{out}} \) pressure fluctuations (\( \tau = 0 \div 10 \)) leads to a decrease of \( c_{\text{out},1}^{\text{ads}} \) by 1-5% in comparison with the concentration \( c_{\text{out},1}^{\text{ads}} \) in the absence of fluctuations (\( \tau = 0 \)).
**Figure 3.** Dependence of oxygen concentration $c_{\text{ads,1}}^\text{out}$ in product flow: a) on the duration of adsorption stage at the pressure during the desorption stage: 1 – $P_{\text{des}}^\text{in} = 0.25 \times 10^5 \text{ Pa}$; 2 – $P_{\text{des}}^\text{in} = 0.5 \times 10^5 \text{ Pa}$; 3 – $P_{\text{des}}^\text{in} = 0.75 \times 10^5 \text{ Pa}$; 4 – $P_{\text{des}}^\text{in} = 1 \times 10^5 \text{ Pa}$; b) on the number of harmonic fluctuations in pressure $P_{\text{ads}}^\text{in}$, $P_{\text{des}}^\text{out}$, $P_{\text{ads}}^\text{out}$ during adsorption stage $t_{\text{ads}}$ : 1 – $P_{\text{ads}}^\text{in}$, 2 – $P_{\text{des}}^\text{out}$, 3 – $P_{\text{ads}}^\text{out}$

**Figure 4.** a) Dependence of oxygen concentration $c_{\text{ads,1}}^\text{out}$ in product flow on: a) pressure $P_{\text{ads}}^\text{out}$ at the temperature of the inlet mixture: 1 – $T_g^{\text{in}} = 0^\circ C$, 2 – $T_g^{\text{in}} = 25^\circ C$, 3 – $T_g^{\text{in}} = 50^\circ C$; b) on the duration of the adsorption stage at: 1 – $T_{\text{env}} = 0^\circ C$, 2 – $T_{\text{env}} = 25^\circ C$, 3 – $T_{\text{env}} = 50^\circ C$

Analysis of the dependence of the oxygen concentration at the outlet of the PSA unit on the pressure and duration of the adsorption stage (Fig. 4) shows that an increase in the temperature of the initial gas-air mixture (Fig. 4a) or external environment temperature (Fig. 4b) from 0 to 50 °C leads to a decrease in the oxygen concentration at the outlet of the PSA unit of ~ 1-4% (vol.) on average (due to a decrease in equilibrium concentration $a_{2,\text{ads}}^\text{out}$ (Equation 6)), but with increasing pressure (Fig. 4a), the oxygen concentration increases (due to an increase in equilibrium concentration $a_{2,\text{ads}}^\text{in}$). The slowing down of the concentration $c_{\text{ads,1}}^\text{out}$ growth (Fig. 4a, curves 1, 2) and its fall (Fig. 4a, curve 3) with increasing pressure above $3.7 \times 10^5 \text{ Pa}$ are caused by an increase in the consumption of the gas-air mixture (Equation 7) and, accordingly, the insufficient regeneration of the adsorption layer (with constant duration of adsorption and desorption stages).
3. Conclusions
In the course of the computational experiments, it was established that: 1) an increase in the reflux ratio of 1.4 times (relative to nominal value $\theta = 2$) leads to an increase in the duration of the adsorption and desorption stages of 2.3 times (relative to nominal values $t_{\text{ads}} = 40 \text{ s}$, $t_{\text{des}} = 40 \text{ s}$); 2) an increase in the adsorption pressure of 2.4 times (with respect to nominal value $p_{\text{ads}}^* = 2.7 \times 10^5 \text{ Pa}$) leads to an increase in the oxygen concentration at the outlet of the unit by 4% (relative to $c_{\text{out},1}^* = 43\%$ (vol.), achieved at nominal values of the variables); 3) an increase in the temperature of the initial gas-air mixture and the external environment temperature by 25 °C (relative to the nominal values of $T_{\text{in}} = 25 \text{ °C}$, $T_{\text{env}} = 25 \text{ °C}$) leads to a drop in the oxygen concentration by 1-4% (vol.) (relative to $c_{\text{out},1}^* = 43\%$ (vol.), achieved at nominal values of the variables). The creation of harmonic pressure fluctuations $p_{\text{des}}^* (n=1)$ or $p_{\text{ads}}^* (n=3 \text{ or } n=6)$ makes it possible to increase the oxygen concentration at the outlet of the PSA unit by ~ 4% (from $c_{\text{out},1}^* = 43.4\%$ (vol.) to $c_{\text{out},1}^* = 47.4\%$ (vol.)), in comparison with the oxygen concentration at the outlet of the unit in the absence of pressure fluctuations. The results of the numerical study will be used to optimize the operation of the PSA unit and the optimal design of oxygen concentrators.

4. Acknowledgments
The work was supported by the Ministry of Education and Science of the Russian Federation under State contract no. 10.3533.2017/PCh.

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