U.P.B. Sci. Bull., Series A, Vol. 68, No. 2, 2006

SEPARATION OF NITROGEN FROM AIR BY SELECTIVE ADSORPTION OF CARBON MOLECULAR SIEVES

Mădălina VĂDUVA, V. STANCIU[*]

Cărbunii sită moleculară (CMS) sunt utilizați la scară largă în procesele de separare a aerului în componentele sale. În această lucrare sunt prezentate rezultatele studiilor experimentale asupra adsorbției cinetice a oxigenului din aer pe CMS utilizând sistemul PSA (adsorbție la presiune variabilă) cu o singură coloană (700 mm lungime, 50 mm diametrul interior).Proprietățile de sită moleculară ale cărbunelui CMS-HP (O_2) preparat în diferite condiții au fost studiate măsurând capacitatea de adsorbție dinamică a O_2. De asemenea, a fost studiată producerea azotului din aer pe CMS-HP(O_2) utilizând un sistem PSA cu două coloane, simplu şi îmbunătățit.

Carbon molecular sieves (CMS) are used on a wide scale for the separation of air into its components. In this paper a brief review is made of the results obtained in recent experimental studies on the sorption kinetics of oxygen from air by CMS used PSA process single column (700 mm length, 50 mm i.d.). The molecular sieves properties of O_2 selective carbon molecular sieves CMS-HP (O_2), prepared under different conditions, were studied by measuring dynamic adsorption capacity from O_2. Also N_2 production from air by CMS-HP (O_2) used PSA (two columns) sample and improved process, were studied.

Keywords: molecular sieves; adsorption; chromatography, coal

Introduction

Air separation is one of the most important applications of PSA (Pressure Swing Adsorption) technology [1-7]. The process, using carbon molecular sieves, was first developed by Bergbau Porschung GmbH and produces Nitrogen of $97 \div 99{,}9\%$ vol. [1]. Separation principle is based on the difference between Oxygen and Nitrogen adsorption speed on CMS. Oxygen, having a smaller diameter of kinetic molecule than that of Nitrogen, diffuses much faster on CMS than Nitrogen. Consequently, we get enriched Nitrogen at adsorbent layer exit.

PSA air separation systems with CMS are mainly used as Nitrogen generators, as Oxygen concentration in the desorbed gas (enriched Oxygen) is of only 30-45 % vol, due to the high partial pressure of Nitrogen in the air ($P_{N_2} = 0{,}78$ as compared to $P_{O_2} = 0{,}21$) [8].

---

[*] Prof., Dept. of Physics, “Ferdinand I” High School, Rm. Vâlcea, Romania; Ph.D Researcher, National R-D Institute for Cryogenics and Isotopic Technologies, Rm. Vâlcea, ROMANIA

The achievement of this procedure of selective adsorbents made of deposit coal (Petrila pitcoal) with features of molecular sieves CMS-HP and the change of their internal structure to increase their selectivity allow the performance of the experiments to enrich Nitrogen in the air by Oxygen selective adsorption within a laboratory PSA system [9].

This paper presents a mathematical model of describing the mass transfer during the selective adsorption in a time variable regime of a component of a binary mixture and the data obtained when applying the model for air Nitrogen enrichment by Oxygen selective adsorption in a PSA column loaded with carbon molecular sieve, CMS-HP (O_2).

The paper also show the data obtained when air Nitrogen is enriched by using experimental PSA system in two variants, a simple one and an enriched one, by recycling between adsorbers.

1. Experiments

1.1. Theoretical Model

Adsorption in a fix layer and dynamic regime is characterised by a continuous flow of fluid phase going through the adsorbent layer in a time variable process.

Fix layer adsorber scheme is shown in Fig. 1.

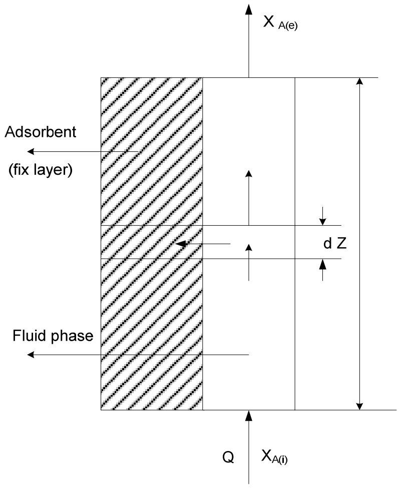

Fig. 1 Model of fix layer adsorbent

Simulation of O_2 adsorption column operation was made by an adsorption model in a time variable regime of a single component of a binary mixture.

At the beginning of the process, the free volume of adsorbent layer is regarded as filled in with a component (B) which cannot be absorbed and that the solid is “clean”, that is without an absorbing component (A). The other simplifying assumptions are: ideal gas, constant temperature in the absorbent layer, constant speed in the section, insignificant pressure drop in the layer.

The mathematical model includes the equations for the adsorbed component in the volume element of dz height, for the fluid phase, and for the solid and the balance equation.

$$\varepsilon \cdot S \cdot C \frac{\partial x_A}{\partial t} = -W_B \frac{\partial x_A}{\partial z} - S(k_x \cdot a) \cdot (x_A - x_{A_0}) \tag{1}$$

$$(1-\varepsilon) \cdot S \cdot dz \cdot \frac{\partial C_{A_S}}{\partial t} = (k_x \cdot a) \cdot (x_A - x_{A_0}) \cdot S \cdot dz \tag{2}$$

$$x_{A_0} = m \cdot C_{A_s} \tag{3}$$

Product ($k_x \cdot a$) stands for the mass transfer coefficient per volume unit of adsorbent layer. Equations (1) and (2) can be simplified by a modified time variable.

$$t' = t - Z\left(\frac{\varepsilon \cdot S \cdot C}{W_B}\right) \tag{4}$$

$$\left(\frac{dx_A}{dz}\right)_{t'} = -\frac{(k_x \cdot a)S}{W_B}(x_A - x_{A_0}) \tag{5}$$

$$\left(\frac{\partial C_{A_s}}{\partial t'}\right)_z = \frac{(k_x \cdot a) \cdot S}{1-\varepsilon} \cdot (x_A - x_{A_0}) \tag{6}$$

Equations (5) and (6) are solved simultaneously, knowing the limit conditions:

- at the initial moment, the concentration of the adsorbed component (A) is zero in any point of the adsorbing layer:

at $t' = 0, C_{As} = 0, for\ z > 0$

- at any moment, A concentration in the gas is constant at layer inlet

at $z = 0, x_A = x_{A_i}, pt\ \ t' > 0$

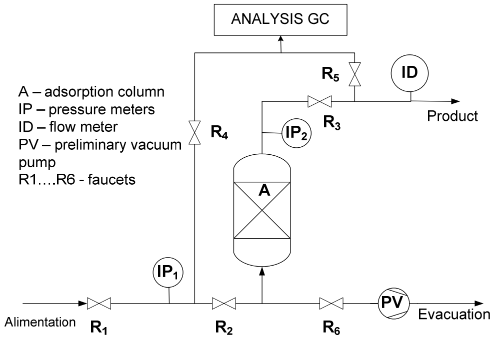

Fig. 2. Experimental testing scheme of selective adsorbents:
A-adsorber; ID-flow rate meter; R1...R6 - tabs; IP-pressure meter; PV- vacuum pump.

1.2. Experimental part of air Nitrogen enrichment process

PSA process of air Nitrogen enrichment includes the following phases:

- air pressurization;
- O_2 adsorption under pressure and getting N_2 as a product;
- depressurization;
- O_2 traces removal by vacuum use.

Adsorption features at O_2/ N_2 separation from air for CMS-HP (O_2) were experimentally established by laboratory PSA system fit with an adsorption column, (Fig. 2) broadly presented in [10] with the specific PSA phases succession.

The experimental system was dynamically operated and its monitoring was made by gas-chromatographic analysis.

Adsorption column is 0.700 m high with an inner diameter of 0.05 m.

Experimental conditions were the following:

- gaps fraction of the adsorbent layer, ε_g = 0.67;
- adsorption column feeding gas: air, with
  - 21% vol. O_2 - component which is adsorbed selectively
  - 78% vol. N_2 - component which is not adsorbed.
- operation temperature: 23°C;
- pressure on adsorption: 4 and 6 bar;
- gas flow rate through adsorber: 25 and 40 L/h;
- duration of selective adsorption: 80 s

Preparation of carbonaceous substrate (Initial CMS - HP)

The pitcoal which was used as carbon precursor for the preparation of CMS was procured from Petrila mine - Hunedoara County, Romania. The experimental procedure followed for the production of CMS is represented by the flow chart shown in Fig. 3.

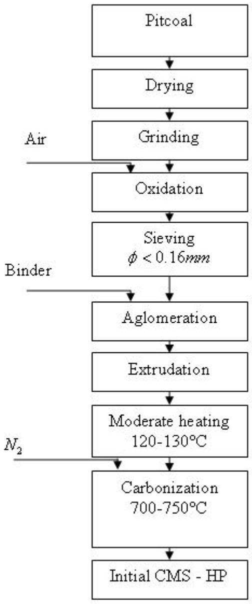

Fig.3 Procedure for the Initial CMS-HP preparation

The pitcoal was first crushed (10 ÷ 30 mm), dried at 150°C for 4 hours and ground to a particle size of 0,5 ÷ 2 mm. This granular mass was subjected to partial air oxidation in fluidised bed at 240 ÷ 250°C, in laboratory device, for 4 ÷ 5 hours. The air flow rate was 40 l/h. Oxidized coal powder was mixed with 11,5 wt% pitch dissolved in benzene and 11,5 wt% starch as binder and then extruded to 6 ÷ 8 mm x 6 mm cylindrical pellets in a pneumatic press. After drying at 120 ÷ 130°C for 4 hours, these pellets were carbonized at 700 ÷ 750°C in N_2 flow for 30 min in the reactor (350 mm length and 50 mm i.d.) with one pre-heater (Fig.4).

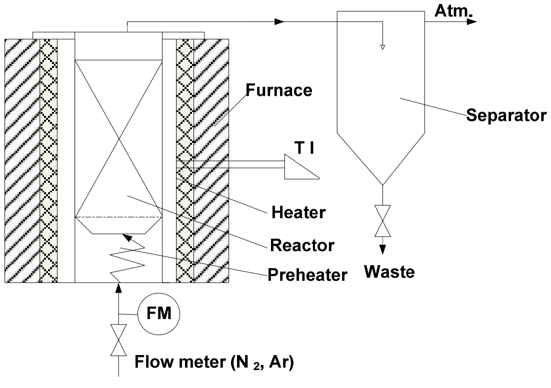

Fig. 4. Schematic diagram of reactor assembly

The N_2 flow rate was $60 \div 80$ l/h and the average heating rate was 5°C/min. After carbonization for a known duration, the heater was switched off and the reactor was allowed to cool in N_2 flow. The product, Initial CMS - HP was removed at room temperature ($25 \div 30$°C).

1.3. Coke deposition by organic polymer cracking

In order to reduce the pore size of initial CMS - HP (carbonaceous substrate), a solution of organic polymer was used as the cracking agent for coke deposition. The aim of coke deposition is to reduce the pore opening to the required molecular range. The sieve character of the initial CMS- HP was improved by impregnation with a 4 wt% solution of polystyrene in benzene. The amount of polymeric impregnator used to block the substrate macropores will vary with the desired gas selectivity. The optional dosage may be determined by varying the dosage and identifying the impregnated sieve with the optional sieving properties. The experimental procedure followed for the modification of Initial CMS-HP by impregnation with a solution of polystyrene in benzene is represented by the flow chart shown in Fig. 5.

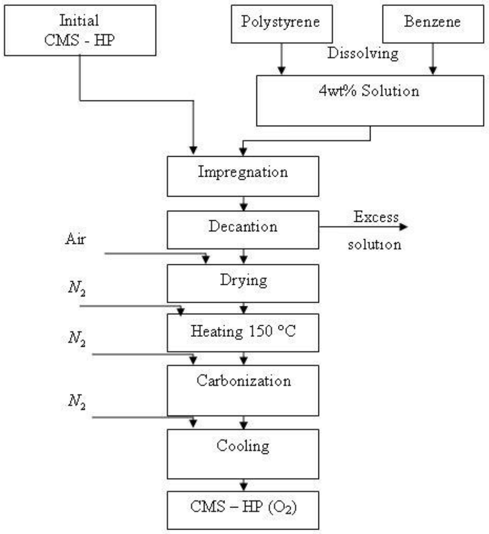

Fig. 5 Procedure for the CMS-HP(O_2) preparation

Carbonaceous substrate (≈ 500 g) was impregnated for two hours with a solution containing 4 wt% polystyrene in 1000 g of benzene. Excess solution was decanted and the substrate was dried in air flow ($40 \div 60$l/h) for $12 \div 16$ hours. After drying, the impregnated substrate was heated for 30 min. at 150°C in the reactor (Fig. 4) and then carbonized at $750 \div 800$°C in N_2 flow ($60 \div 80$ 1/h) for 30 min. The average heating rate was 5°C/min. After carbonization, the heaters were switched off and the reactor was allowed to cool in N_2 flow. The product, CMS - HP(O_2) was removed at room temperature (25 ÷30°C).

1.4. Adsorption measurement

Performance tests for separation of O_2/N_2 from air on CMS - HP (O_2) were carried out by using a PSA single adsorber with 200 mm length and 50 mm i.d. (Fig. 6).

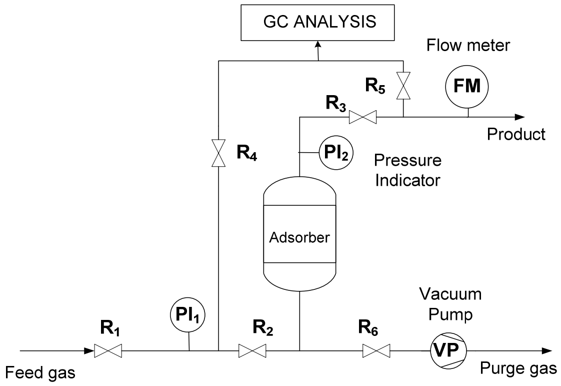

Fig. 6. Flow sheet of the PSA - test apparatus

The complete cycle of a laboratory PSA consists of the following steps:

- pressurization of the adsorber with feed gas (air);
- adsorption and production of N_2;
- counter - current depressurization;
- evacuation by vacuum pump.

The initial gas (air) and the samples collected were analysed by GC with thermal conductivity detector (TCD) using Molecular Sieve column at oven and detector temperatures of 100°C and 120°C respectively. The influence of the operating parameters (pressure and flow rate) on the breakthrough curves was investigated. Dynamic adsorption capacity for O_2 was measured in the pressure range 2 ÷10 bar and calculated with the formula:

$$a = \frac{Q \cdot p(C_i - \overline{C_e}) \cdot t}{m} \tag{7}$$

where:

a - dynamic adsorption capacity (cm^3/g)

Q - gas exit flow rate (cm^3/s);

p - adsorption pressure (bar);

C_i - O_2 feed concentration (fraction %);

$\overline{C_e}$ - mean O_2 concentration up to breakthrough at adsorber exit (fraction %);

t - the breakthrough time (s);

m - utilized CMS quantity (g).

Separation efficiency was calculated by

$$\eta = \frac{C_a}{C_i} \cdot 100 \tag{8}$$

where:

η - separation efficiency (%);

C_a - concentration of O_2 adsorbed (vol.%);

C_i - O_2 feed concentration (vol.%).

1.5. Nitrogen recovery from air

After previous laboratory tests the N_2 - PSA process was made in an experimental plant. The flow diagram of the simple plant is shown in Fig. 7.

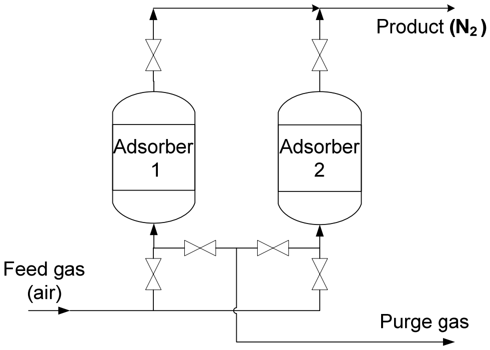

Fig. 7. Flow sheet of the experimental simple N_2 -PSA plant

Two adsorbers (700 mm length and 72 mm i.d.) are filled with CMS - HP (O2) and equipped with incoming air pipes and outgoing nitrogen pipes and valves. Air compressed to 4 bar enters the CMS -HP(O_2) bed in one adsorber. On passing over the CMS - HP (O_2), O_2 is adsorbed and nitrogen leaves the adsorber.

Operating conditions of experimental plant was:

- adsorption pressure: 4 bar;
- temperature: ambient;
- gas exit flow rate: 10 ÷ 100 l/h;

- adsorption time: 1 min.;
- desorption pressure: $6 \div 8 \cdot 10^{-2}$ bar.

During adsorption in one adsorber, a second adsorber is regenerated by reducing the pressure to ambient pressure and vacuum application. After a certain adsorption time ($1 \div 2$ min.), the O_2 starts to breakthrough the CMS bed at the top of the adsorption vessel. At this stage the adsorption step is stopped. Nitrogen is recovered during the adsorption phase, while an O_2 - enriched waste gas ($30 \div 35$ vol.% O_2) is produced in the desorption phase (depressurization).

Because of the pressure differences between adsorption and desorption, significant pressure losses at desorption and the relatively short cycle times, precise requirements are imposed on the technical design of N_2 - PSA. Therefore, before starting the adsorption step in the second adsorber, a pressure equalizing step of both adsorbers is necessary in order to pre-pressure the second adsorber. The flow diagram of the optimized N_2 - PSA plant is shown in Fig. 8.

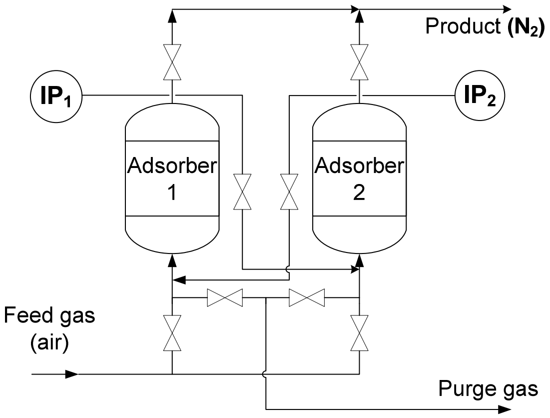

Fig. 8. Flow sheet of the optimized N_2-PSA plant

The samples collected were analysed by GC with TCD. Using the concentration values were calculated:

Separation efficiency (η) by formula (8);

- Nitrogen recovery, by

$$R_{N_2} = \frac{\overline{C_{e(N_2)}} - C_{i(N_2)}}{C_{i(N_2)}} \cdot 100 \tag{9}$$

where:

R_{N_2} - Nitrogen recovery, %;

$\overline{C}_{e(N_2)}$ - means N_2 concentration up to breakthrough at adsorber exit, fraction %;

$\overline{C}_{i(N_2)}$ - N_2 feed concentration, fraction %.

- Productivity, cm^3 N_2/cm^3 CMS-HP(O_2)- h which was calculated for every gas exit flow rate. To produce purity N_2 was used a N_2-PSA plant with additional after -cleaning using copper as an O_2-reducing reactant, Fig. 9.

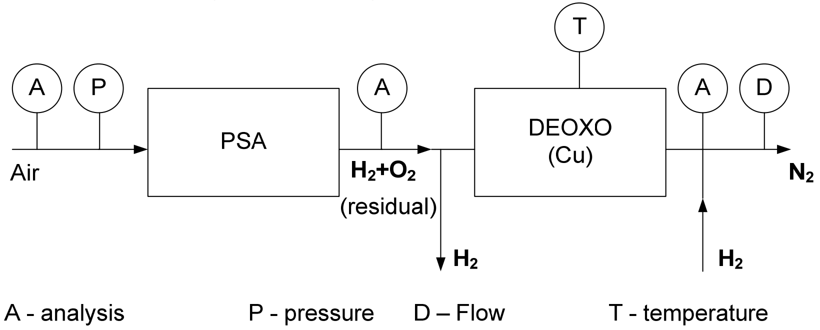

Fig. 9. Scheme for a N_2-PSA+ DEOXO system

The deoxo unit needs one external heated reactor filled with copper for the endothermic reaction:

$$O_2 + 2Cu \xrightarrow{550^\circ C} 2CuO$$

The loaded cooper can be regenerated by adding H_2 during the regeneration step. For this two - step process (deoxidation and regeneration), two reactors are necessary to achieve a continuously operating deoxo system. The N_2 from the PSA plant with the remaining O_2 passes the heated reactor without adding hydrogen. On passing through the reactor, the O_2 is removed by reacting with the copper surface. The remaining heat can be reduced by a standard after / cooler to the required level. The advantage of the deoxo unit based on cooper in comparison with the deoxo unit using palladium on platinum as a catalyst is that the purity N_2 leaves the unit dry and without any remaining hydrogen.

2. Results and discussions

2.1 Results and discussions on adsorption model in a time variable regime

Adsorbent performance during dynamic separation is characterized by the transfer coefficient ($k_x \cdot a$). This parameter was established based on the theoretical model shown above. The theoretical curve can be calculated if we know the balance constant value (m). This is found out by making the adsorption isotherm linear:

$$C_{O_2(s)} = f(x_{O_2(e)}) \tag{10}$$

Oxygen concentration in adsorbent is calculated by means of experimentally established measures:

$$C_{O_2(s)} = \frac{Q}{3600} \cdot \tau \cdot \frac{x_{O_2,i} - x_{O_2,e}}{V_m \cdot V_{layer}} \tag{11}$$

The line slope, approximating best experimental points, is the balance constant (m). Figs. 10 a, b, c show the adsorption isotherms experimentally established and the straight lines approximate them best.

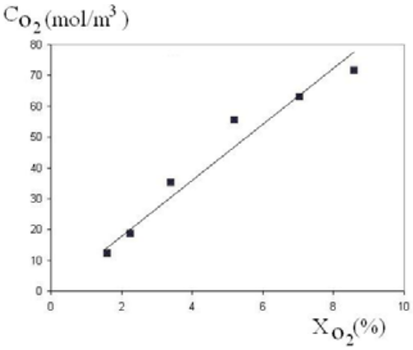

Fig. 10 a

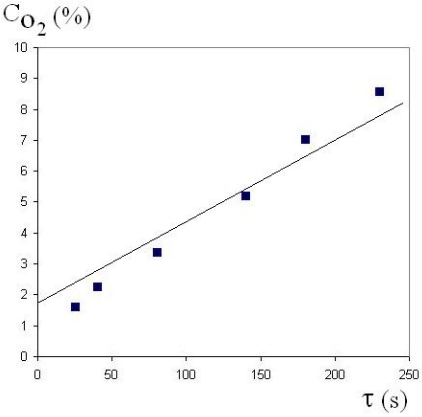

Fig. 11 a

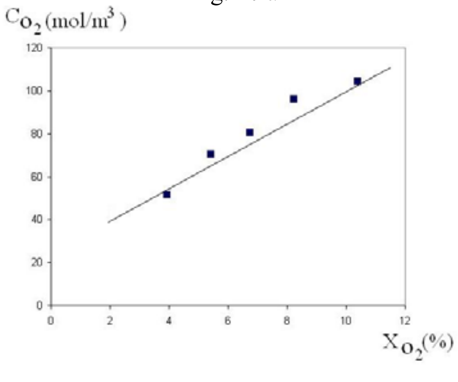

Fig. 10 b

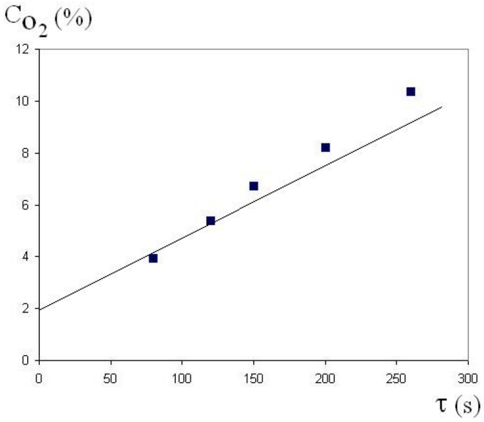

Fig. 11 b

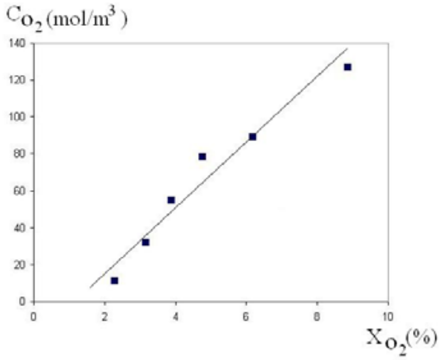

Fig. 10 c

Fig. 10. O $_2$ concentration variation in column exit gas: a→ p=4 bar, G=25L/h; b → p=6 bar, G=25L/h; c→ p=4 bar, G=40 L/h
□ → measured values; —— → theoretic curve

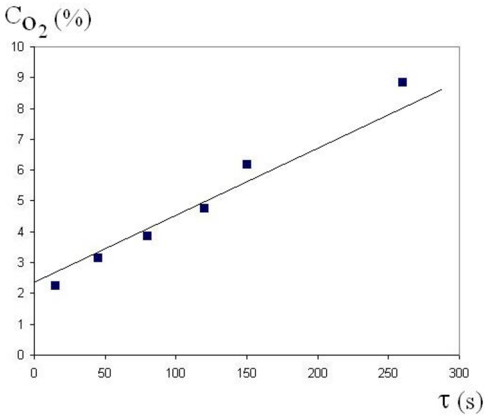

Fig. 11 c

Fig. 11. O $_2$ concentration time variation in the adsorbent layer according to O $_2$ concentration in column exist gas:
a→ p=4 bar, G=25L/h; b→ p=6 bar, G=25L/h; c→ p=4 bar, G=40 L/h.
□→ experimentally established,
——→ experimental data made lineal

The transfer coefficient was established as follows: theoretical variation curves in time were calculated for Oxygen concentration at column exit, giving the transfer coefficient several values; the real value was taken as the one for which the theoretical curve approximated best experimental points.

Theoretical curves of concentration time variation were obtained by solving the system of equations (5) and (6) by Euler numerical method. Adsorbent layer was divided in 20 elements and the time interval taken for repetitions was of one second.

The graphs in Fig. 11 a, b, c show the theoretical curves approximating best the time variation of Oxygen concentration in the gas flow at adsorber exit.

Symbols

ε - gaps fraction of adsorbent layer;

S – column cross section area;

C_{A_s} - molls of adsorbed component in solid volume unit, mol/m^3;

X_A - molar fraction of A component in the fluid;

X_{A_0} - molar fraction of A component at gas-solid interface, regarded as being in balance with C_{A_s};

k_x – mass transfer coefficient per unit of adsorption surface, mol/m^2·s;
a - specific surface of adsorbent layer, m^2/m^3;
C – fluid molar concentration, mol/m^3;
w_B – molar flow rate of B component, mol/s;
t - time, s;
Z - length of adsorbent layer, m;
S - column cross section area, m^2;
m – balance constant, m^3/mol;
$C_{O_2(s)}$ - O_2 concentration in adsorbent layer, mol/m^3;
Q – gas flow rate, L/h;
τ - adsorption time, s;
$X_{O_2,i}$, $X_{O_2,e}$ - O_2 concentration in fed/exit gas flow into/from adsorber, fr. mol;
V_m - molar gas volume, L/mol;
V_{layer} – adsorbent layer volume (L).

2.2 Results and discussions on air Nitrogen separation by selective adsorption on CMS

The general properties of CMS-HP(O_2) were measured using the pycnometric method. The results are given in Table 1.

Table 1.

General properties of CMS-HP(O_2)

CMS - HP (O_2)	
Apparent density (g/cm^3)	0,96
True density (g /cm^3)	1,42
Packed density (g /cm^3)	0,47
Porosity (cm^3 / cm^3)	0,33
Void fraction	0,67
Pore volume (cm^3 /g)	0,35

Separation specific parameters of O_2 by selective adsorption on CMS-HP (O_2) at elevated pressure (2 $\div$ 10 bar) are presented in Table 2.

Table 2.

Separation specific features of O_2

Adsorption pressure (bar)	Dynamic adsorption capacity, a (cm^3/g)	O_2 adsorption efficiency, η (%)	The breakthrough time, t (s)	Concentration up to breakthrough at adsorber exit (vol. %)	
				(O_2 + Ar)	N_2
2	0,20	80,50	80	3,20 ÷ 4,80	95,80 ÷ 94,22
4	0,47	82,38			
6	0,61	80,90			
8	0,82	80,90			
10	1,02	80,47			

Summary of the simple N_2- PSA experimental conditions, product purity, O_2 separation efficiency, N_2 recovery and productivity are presented in Table 3.

Table 3.

O_2/N_2 separation from air (simple N_2- PSA)

Exp. no.	Q (1/h)	v ($m/s \cdot 10^{-2}$)	Concentration in product (vol. %)			O_2 adsorption efficiency (%)	N_2, recovery (%)	Productivity ($cm^3 N_2/cm^3$ CMS · h)
			O_2 + Ar	O_2	N_2			
1.	10	0,14	4,92	3,99	95,07	81,00	21,88	6,78
2.	20	0,28	5,01	4,08	94,98	80,57	21,76	13,42
3.	30	0,42	5,25	4,32	94,74	79,42	21,46	20,35
4.	40	0,56	5,38	4,45	94,61	78,80	21,29	27,03
5.	50	0,69	5,43	4,50	94,56	78,57	21,23	33,77
6.	60	5,43	4,50	4,50	94,56	78,57	21,23	33,77
7.	70	0,97	5,60	4,67	94,39	77,76	21,01	47,19
8.	80	1,10	5,90	4,97	94,09	76,33	20,62	53,76
9.	90	1,30	5,80	4,90	94,19	76,66	20,75	60,55
10.	100	1,40	6,58	5,65	93,41	73,09	19,75	66,72

Also, summary of the optimized N_2 - PSA experiments are presented in Table 4.

Table 4

O_2/N_2 separation from air (optimized)

Exp. no.	Q (1/h)	v ($m/s \cdot 10^{-2}$)	Concentration in product (vol. %)			O_2 adsorption efficiency (%)	N_2, recovery (%)	Productivity (cm^3 N_2/cm^3 CMS · h)
			O_2 + Ar	O_2	N_2			
1.	10	0,14	0,96	0,03	99,03	99,76	26,96	7,07
2.	20	0,28	1,07	0,14	98,93	98,93	26,82	14,13
3.	30	0,42	1,15	0,22	98,84	98,30	26,71	21,18
4.	40	0,56	1,24	0,31	98,75	97,62	26,65	28,24

5.	50	0,69	1,13	0,20	98,86	98,46	26,74	35,31
6.	60	5,43	1,50	0.57	98,49	95,61	26,26	42,21
7.	70	0,97	1,62	0,63	98,37	95,15	26,11	49,18
8.	80	1,10	2,05	1,12	97,94	91,38	25,56	55,96
9.	90	1,30	3,89	2,96	96,70	77,23	23,94	62,16
10.	100	1,40	6,14	5,21	93,85	59,92	20,32	66,78

The gas flow velocity through the CMS - HP (O_2) bed determines the remaining O_2 concentration in the N_2 produced. By changing this velocity, the O_2 concentration can be adjusted between $0,03 \div 5,20$ vol.%.

In Table 5 are presented experimental data for N_2- PSA plant with additional deoxo system.

Table 5

Experimental data for the N_2- PSA + Deoxo system

Exp. No.	Q (l/h)	v ($m/s \cdot 10^{-2}$)	O_2 concentration in product (vol. %)		N_2 concentration in product (vol. %)	
			PSA exit	Deoxo exit	PSA exit	Deoxo exit
1.	10	0,14	3,04	0,45	96,95	99,54
2.	20	0,28	3,15	0,50	96,84	99,49
3.	30	0,42	3,26	0,55	96,73	99,44
4.	40	0,56	3,40	0,47	96,59	99,52
5.	50	0,69	3,48	0,54	96,51	99,45
6.	60	5.43	3.86	0,50	96,13	99,49
7.	70	0,97	3.93	0,52	96,06	99,47
8.	80	1,10	4,44	0,54	95,55	99,45
9.	90	1,30	4,57	0,42	95,42	99,57
10.	100	1,40	5,43	0,47	94,59	99,52

The N_2 concentration after N_2 - PSA plant decrease from 96,95 vol. % at 94,56 vol. % when gas exit flow increases from 10 1/h at 100 1/h. After deoxo system for all gas exit flow range, the N_2 is obtained with a purity of more than 99,45 vol.%. The flexibility of N_2 - PSA system with regard to flow rate and purity makes it easy to meet the requirements on the consumer's side.

Conclusions

In order to mathematically describe the Oxygen selective adsorption process performed to enrich air Nitrogen, we used adsorption model in time variable regime of a component from a binary mixture.

The model allows us to establish the transfer coefficient characterising adsorbent performance in a dynamic regime.

The experimental data were obtained within ICSI in laboratory PSA system, with adsorbents obtained by our own procedure from deposit coal.

The theoretical curves obtained based on this model approximate well the time variation of Oxygen concentration at adsorbent exit.

The results demonstrate that Carbon Molecular Sieves for O_2/N_2 separation from air can be prepared from Romanian pitcoal. In order to further reduce the pore size, a carbon deposition technique was used by carbonaceous substrate impregnation with a solution; of polystyrene and carbonization in N_2 atmosphere at $750 \div 800°C$. The separation specific parameters of O_2 by selective adsorption on CMS - HP (O_2) indicate their suitability for packing N_2-PSA columns. To produce purity N_2 can be used a N_2 -PSA plant with additional after - cleaning system using deoxo process.

REFERENCES

1. *T.C. Golden, P.J Battavio., Y.C. Chbn, T.S. Farrjs and JN. Armor* , Gas Separation and Purification, **vol VII**, nr. 4, 1993, p. 274
2. *J.N. Armor*, Molecular Sieves for Air Separation Materials Chemistry; An Emerging Discipline - American Chemical Society 1995
3. *** Nitrogen, Pulled right out of thin air - Carbotech, Industrieservice GmbH, Essen, Germany nr. 1993/12, 1994
4. *Shivaji, Sircar*, Pressure Swing Adsorption; Research Needs by Industry, Proceedings of 3rd International Conference of Fundamentals of Adsorption, Germany, 1991, p. 815
5. *G.H. Baron*, Industrial Gas Separation Using PSA - in Separation Technology, p. 201 edited by E.F. Vansant, Elsevier Science B.V. Amsterdam 1994
6. *Shivaji, Sircar*, Gas Separation and Purification, **vol VII**, nr. 2, 1993
7. *H.J. Schroter* - Gas separation and Purification, **vol VII**, nr. 4, 1993, p. 247
8. *H.J Schroter*, Gas Separation and Purification, **vol VII**, nr. 4, 1993, p. 274
9. *V. Stanciu, D. Ştefănescu*, Chem. Rew. (Bucharest), **vol 47**, nr. 7, 1996, p. 655
10. *V. Stanciu, E. David, D. Ştefănescu*, Chem. Rew. (Bucharest), **vol 46**, nr. 4, 1995, p. 344