THE USE OF THE THEORY OF STATISTICAL MOMENTS FOR A DESCRIPTION AND EVALUATION OF NOBLE GASE BREAKTHROUGH IN CARBON ADSORBENT BEDS

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The values of the first-fourth statistical moments have been determined of the argon, krypton and xenon breakthrough curves, which were measured on the active carbon Supersorbon HS and the carbon adsorbent Jado LD 1191 beds, at temperatures 298–473 K, by means of elution gas chromatography. The application of the Gram-Charlier series – including the first-fourth statistical moments – enabled to describe satisfactorily the breakthrough curves over the whole range of outlet concentrations of the studied gases. On the basis of the theory of statistical moments, selected parameters, characterizing the dynamic adsorption in the studied systems were determined. The obtained parameters allowed to compare and evaluate the properties of the adsorption beds of both adsorbents – especially with respect to their possible use as a packing in the delaying line units of radioactive noble gases.

An evaluation of the function of the delaying line adsorption beds used in nuclear power plants for separation of radioactive noble gases from the effluents, requires to know the values of a large number of parameters describing the adsorbent–adsorbate system. These parameters are related to the character of the adsorption isotherms, the mobile phase flow, the geometrical properties of the bed *etc.* and they determine, therefore, the distribution of the adsorbate in the bed and consequently also the bed separation efficiency. In the previous paper[1], we have published the basic parameters for the adsorption of the noble gases on active carbon Supersorbon HS and the carbon adsorbent Jado LD 1 191 (derived from the adsorption isotherms).

The present paper is concerned with evaluation of the adsorption properties of the above adsorbents, which is based on the description and analysis of the breakthrough curves of argon, krypton and xenon. The linear character of the argon, krypton and xenon adsorption isotherms obtained, under the given conditions, for the studied carbon adsorbent[1] – permitted to evaluate the adsorption dynamics of the studied systems by means of the theory of statistical moments[2–4]. This theory provides quantitative information on the adsorbate breakthrough in the bed, in the form of statistical moments of the breakthrough curves, which are found – for the given case – to be quite sufficient for determination of the basic parameters of the adsorption beds – regardless whether the actual mechanism of the mass transport is known or not. In addition, as it is shown in paper[5], this theory provides a wide range of possibilities to analyze the breakthrough of all radiactive isotopes of the given

noble gas – knowing just one single breakthrough curve of the stable isotope which was obtained at comparable conditions. This approach can be with advantage used in practical designs of the noble gas delaying line units.

EXPERIMENTAL

The quantities used in this paper for the description of dynamic adsorption of argon, krypton and xenon in Supersorbon HS and the Jado LD 1191 beds were derived from experimental elution curves measured at temperatures 298·15; 323·15; 373·15; 423·15 and 473·15 K. The experimental arrangement, the conditions and the procedure of measurement of the elution curves were described – together with the physical parameters of the adsorption beds – in the preceeding paper[1].

The values of the first ordinary statistical moments (m_1) and the second-fourth central statistical moments (m_2, m_3, m_4) were determined from the elution curves in the way described in paper[6] and they have been used – in accordance with their physical meaning[2-3] – for further analysis of the breakthrough curves.

TABLE I
The reduced statistical moments for Supersorbon HS

T, K	m_k^0	Ar	Kr	Xe
298·15	m_1^0	101	422	6 663
	m_2^0	68·3	573	$1{\cdot}534 \cdot 10^5$
	m_3^0	379	3 909	$1{\cdot}09 \cdot 10^7$
	m_4^0	2 561	$1{\cdot}52 \cdot 10^5$	$2{\cdot}02 \cdot 10^{10}$
323·15	m_1^0	92·3	335	2 746
	m_2^0	42·6	539	28 697
	m_3^0	237	62 333	$1{\cdot}06 \cdot 10^6$
	m_4^0	917	$2{\cdot}23 \cdot 10^5$	$8{\cdot}42 \cdot 10^8$
373·15	m_1^0	64·1	157	1 033
	m_2^0	34·1	113	5 076
	m_3^0	242	903	$1{\cdot}07 \cdot 10^5$
	m_4^0	576	14 801	$2{\cdot}07 \cdot 10^7$
423·15	m_1^0	51·2	94·2	388
	m_2^0	28·0	49·1	850
	m_3^0	174	235	21 243
	m_4^0	376	2 540	$2{\cdot}5 \cdot 10^5$
473·15	m_1^0	43·9	69	209
	m_2^0	47·9	75·0	257
	m_3^0	622	1 094	7 480
	m_4^0	1 622	16 424	$1{\cdot}35 \cdot 10^5$

The argon, krypton and xenon frontal breakthrough curves (*i.e.* the dependence of relative outlet concentration C/C_0 on breakthrough time) were derived from the elution curves by means of their numerical integration.

The analytical description of the breakthrough curves by their statistical moments — which is necessary for a further generalization and interpretation of the experimental data — was carried out using the Gram–Charlier series[4], which gives for the first-fourth statistical moments the following expression for the breakthrough time of the gas with relative concentration C/C_0 at the outlet of the adsorption bed:

$$t = m_1 + \sqrt{(m_2)} \, . \, t_c + (m_3/6m_2)\,(t_c^2 - 1) - (t_c \sqrt{(m_2)}/24)\,(m_4/m_2^2 - 3)\,(t_c^2 - 3)\,, \qquad (1)$$

where t_c is the argument of the integral of normal distribution, the value of which equals C/C_0.

Comparison of the experimental and the calculated parameters of breakthrough curves (given in detail in paper[7]) has proved that the above mentioned analytical description of experimental breakthrough curves is quite satisfactory for the whole range of relative gas outlet concentrations. The differences between the calculated and the experimental parameters of breakthrough curves

TABLE II

The reduced statistical moments for Jado LD 1191

T, K	m_k^0	Ar	Kr	Xe
298·15	m_1^0	28·8	57·9	436
	m_2^0	22·8	32·2	2 767
	m_3^0	308	484	$2{\cdot}52 \, . \, 10^5$
	m_4^0	196	739	$1{\cdot}49 \, . \, 10^7$
323·15	m_1^0	27·1	45·7	240
	m_2^0	29·1	26·5	778
	m_3^0	447	304	37 791
	m_4^0	332	639	$9{\cdot}72 \, . \, 10^5$
373·15	m_1^0	24·5	32·4	89·1
	m_2^0	38·2	28·6	133
	m_3^0	633	414	3 112
	m_4^0	533	597	31 082
423·15	m_1^0	23·4	28·0	50·0
	m_2^0	44·2	46·2	61·5
	m_3^0	802	862	1 163
	m_4^0	679	1 178	3 720
473·15	m_1^0	24·2	27·5	39·7
	m_2^0	60·3	55·7	67·2
	m_3^0	1 327	1 152	1 299
	m_4^0	1 269	1 728	4 346

vary in the range 0—5% and only scarcely — at the boundary concentrations — they become greater than 10%

RESULTS AND DISCUSSION

The experimental values of the first-fourth statistical moments and the dynamic adsorption parameters derived from them cannot be used directly for comparison of the properties of the studied beds, since they are not related to the same geometric and flow conditions (see ref.[1], Table I). For this reason, these values were transformed to "reduced" statistical moments, related to a unit length of the adsorption bed $L^0 = 1$ m and to a unit flow rate $u^0 = 0{\cdot}1$ m s^{-1}.

The way of reduction of the statistical moments (which uses the analytical expressions for calculation of the statistical moments, applying the physical and geometrical bed parameters[3]) is illustrated by the following reduction of the first and the second statistical moments. Since all the physical and geometrical parameters of the reduced bed (with the exception of the length of the bed and the flow rate) remain unchanged with respect to the original bed — the equations for evaluation of the first and the second statistical moments[3] can be rewritten to a form

$$m_1 = x_1 \, . \, a \, , \tag{2}$$

$$m_2 = x_2(x_1 + x_2)\, a^2 + 2x_1 b \, , \tag{3}$$

where a and b are constants (involving the non-changing parameters of the adsorption bed and of the sorbed gas), which depend only on the temperature. On the other hand, quantities x_1 and x_2 depend on the length of bed L, the flow rate u and indirectly on the temperature through the effective diffusion coefficient D_p, as can be seen on the following expressions:

$$x_1 = L/u + 2D_p/u^2 \, , \tag{4}$$

$$x_2 = 2D_p/u^2 \, . \tag{5}$$

In a similar way it is possible to express also the reduced moments m_1^0 and m_2^0, for which it holds

$$m_1^0 = a x_1^0 \tag{6}$$

$$m_2^0 = x_2^0(x_1^0 + x_2^0)\, a + 2x_1^0 b \, , \tag{7}$$

where the constants a and b preserve their original meaning and the quantities x_1^0 and x_2^0 depend on the reduced bed length L^0, the reduced flow rate and the tempera-

ture. Solution of the above equations for the original and for the reduced conditions in the adsorption bed leads to the first and to the second reduced statistical moments. In the same way are derived and solved the expressions for the third and the fourth reduced moments. The calculated values of all reduced moments for argon, krypton, xenon – for Supersorbon HS and Jado 1191 beds – are presented in Tables I and II.

The reduced statistical moments enabled to analyze and compare the breakthrough of the studied noble gases in the Supersorbon HS and Jado LD 1191 beds, using preferentially the breakthrough curves of the reduced beds, their normalized statistical moments and the capacities of both adsorption beds.

The Breakthrough Curves

Applying the values of the reduced statistical moments and the expression (*1*) (the suitability of which for description of experimental breakthrough curves was proved in paper[7]), we have calculated the breakthrough curves of argon, krypton and xenon for the reduced Supersorbon HS and the Jado LD 1191 beds – considering gas outlet concentrations $C/C_0 = 0{\cdot}002 - 0{\cdot}998$ and temperatures in the range 298·15 – 473·15 K.

TABLE III
The normalized moments

Gas	T, K	Supersorbon HS		Jado LD 1191	
		$m_2^0/(m_1^0)^2 \cdot 10^3$	$m_3^0/(m_2^0)^{3/2}$	$m_2^0/(m_1^0)^2 \cdot 10^2$	$m_3^0/(m_3^0)^{3/2}$
Ar	298·15	6·7	0·67	2·7	2·82
	323·15	5·0	0·85	3·9	2·85
	373·15	8·3	1·21	6·4	2·86
	423·15	10·7	1·18	8·1	2·73
	473·15	24·8	1·87	10·3	2·83
Kr	298·15	3·2	0·29	0·96	2·65
	323·15	4·8	0·50	1·3	2·23
	373·15	4·5	0·75	2·7	2·70
	423·15	5·5	0·68	5·9	2·75
	473·15	19·5	1·18	7·4	2·77
Xe	298·15	3·5	0·18	1·5	1·73
	323·15	3·8	0·22	1·4	1·74
	373·15	4·8	0·30	1·7	2·03
	423·15	5·6	0·86	2·5	2·41
	473·15	5·9	1·82	4·3	2·36

As can be seen in Figs 1–6, the curves differ both in their positions along the time coordinate and in the character of their time-courses. The breakthrough times of argon, krypton and xenon, with Supersorbon HS, exceed largely the corresponding values for Jado LD 1191 – especially in the low and the medium range of relative outlet concentrations (*e.g.* at 298·15 K: 3 times with argon, 7 times with krypton and up to 15 times with xenon).

With increasing temperature, these differences become smaller (the lighter the gas, the smaller are the differences), as can be seen from the comparison of the first reduced moments in Tables I and II.

The observed differences in the character of the breakthrough curves of the above gases, in both beds, can be demonstrated on the values of the second and the third normalized moments, as it is shown in Table III. The mutual comparison of the normalized moments for both types of adsorbents shows that the broadening and the asymmetry of the breakthrough curves is much higher with the Jado LD 1191 adsorbent. For both types of adsorbents, the asymmetry and the broadening of the curves increases with the raising temperature.

The second normalized moment gives – after it has been multiplied by the length of the column – the height of the theoretical plate or the transfer zone depth and, in this form, it characterizes the separation efficiency of the bed. From Table III, it is evident that the separation efficiency is for all gases and at all temperatures better with the Supersorbon HS bed than with the Jado LD 1191 bed. The height of the theoretical plate for the Supersorbon HS bed is in average about four times

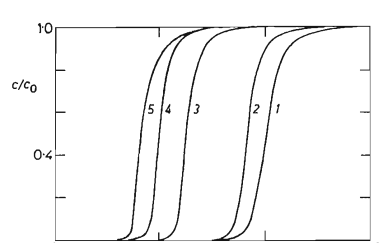

FIG. 1

The breakthrough curves of argon for Supersorbon HS reduced beds *1* 298·15 K; *2* 323·15 K; *3* 373·15 K; *4* 423·15 K; *5* 473·15 K

lower than that of the Jado LD 1191 bed and it varies between 0·7 – 2·5 cm for argon, 0·3 – 2·0 cm for krypton and 0·3 – 0·6 cm for xenon.

Capacity of the Beds

The capacity of the Supersorbon HS and Jado LD 1191 adsorption beds (real E_r and ideal E_i) can be, in the given case, with convenience evaluated using the expres-

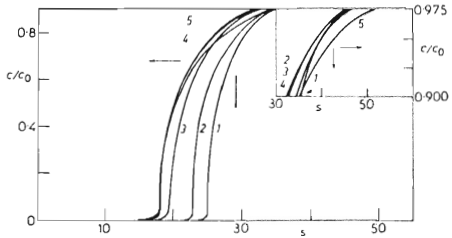

FIG. 2

The breakthrough curves of argon for Jado LD 1191 reduced beds (denotation of the curves as in Fig. 1)

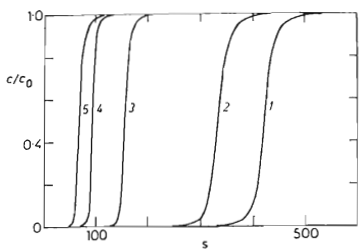

FIG. 3

The breakthrough curves of krypton for Supersorbon HS reduced beds (denotation of the curves as in Fig. 1)

sions defined by Grubner[4]

$$E_i = C_0 F m_1 , \tag{8}$$

$$E_r = C_0 F t(C/C_0) \tag{9}$$

because these expressions relate the adsorption properties of the bed with its basic operation parameters, such as the volumetric flow rate F, the inlet concentration C_0 and the temperature of the bed.

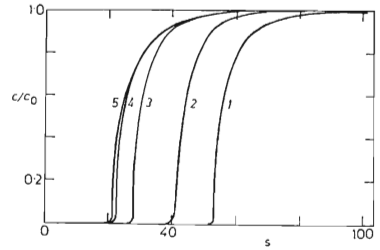

FIG. 4

The breakthrough curves of krypton for Jado LD 1191 reduced beds (denotation of the curves as in Fig. 1)

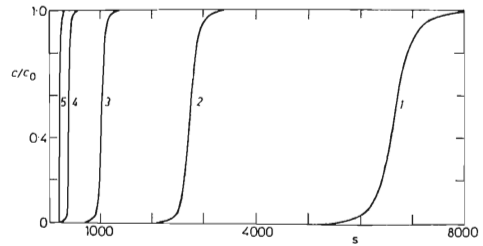

FIG. 5

The breakthrough curves of xenon for Supersorbon HS reduced beds (denotation of the curves as in Fig. 1)

In agreement with the positions and forms of breakthrough curves of the individual gases, the obtained results show that the ideal capacity (characterized only by the first moment of the breakthrough curve), so as the real capacity (accounting for time distribution of the adsorbate concentration at the bed outlet), are much higher with Supersorbon HS than with Jado LD 1191. The quantitative relation between the capacities of both beds is immediately evident from the comparison of the breakthrough curves in Figs 1–6.

Besides the absolute values of the real and the ideal bed capacities, great importance is given also to the corresponding relative values – representing the ratio of the real and the ideal capacity or the capacity loss $Z = 1 - E$. Practical importance of the relative capacity and the capacity loss values is connected with the fact that they both permit to determine, during the testing of the delaying lines with stable gases, the loading factor of the studied bed – for the required gas breakthrough degree under relevant operation conditions. Both the above parameters offer therefore a suitable complementary criterion for selection of the proper adsorbent – especially in such cases when the breakthrough curves of the compared beds differ only slightly in their first statistical moments.

The dependence of relative capacity (loss of capacity) of the Supersorbon HS and Jado LD 1191 beds on the relative outlet concentrations of the studied gases can be seen, for temperatures 298·15 and 473·15 K, in Figs 7–9. The analysis of these dependences shows that in the region of the very low noble-gas concentrations – which is of special interest for practical applications of the adsorption beds – the

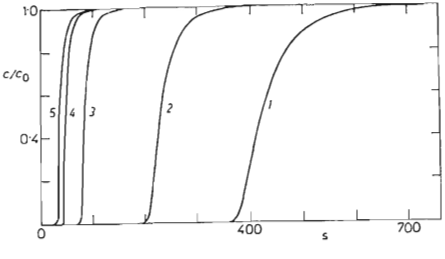

FIG. 6

The breakthrough curves of xenon for Jado LD 1191 reduced beds (denotation of the curves as in Fig. 1)

real capacity represents only about 60–80% of the ideal capacity. On the other hand, with relative outlet concentrations higher than 0·7 – the real capacity exceeds the ideal capacity by 100–200%, depending on the required breakthrough degree, the type of gas, the adsorbent and the temperature. From Figs 7–9, it is also evident that the differences between the ideal and the real bed capacity are much more pronounced in the Jado LD 1191 beds than in the Supersorbon HS beds.

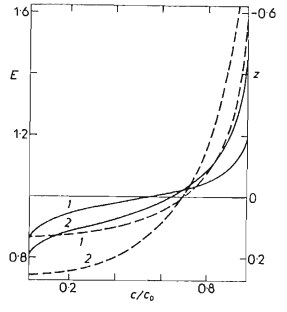

FIG. 7

The dependence of relative capacity and capacity loss of reduced beds on the argon outlet concentration: ——— Supersorbon HS, – – – – – Jado LD 1191; *1* 298·15 K; 2 473·15 K

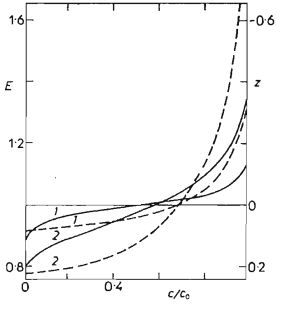

FIG. 8

The dependence of relative capacity and capacity loss of reduced beds on the krypton outlet concentration (denotation of the curves as in Fig. 7)

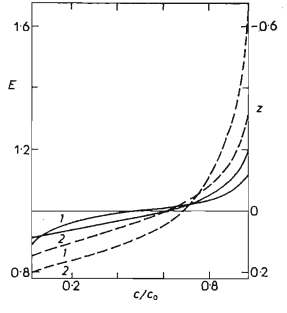

FIG. 9

The dependence of relative capacity and capacity loss of reduced beds on the xenon outlet concentration (denotation of the curves as in Fig. 7)

One can conclude that the results presented in this paper show large differences in the adsorption properties of the both studied beds. While the amount of adsorbed argon, krypton and xenon (given by the slopes of adsorption isotherms – determined in our previous paper[1]) characterize in the case of the Jado LD 1191 adsorbent only the properties of the carbon surface layer covering the teflon support – the reduced moments and the corresponding positions and courses of the breakthrough curves, as well as the bed capacities, describe the bed as the whole, *i.e.* they include the teflon material. For this reason, the differences observed for the dynamic adsorption parameters of both types of adsorbents are much more distinct than the differences in the adsorbed amounts. If it were technically possible to prepare the Jado carbon adsorbent without a teflon support, yet, with the same mechanical parameters, one could expect that the favoutable adsorption properties of this adsorbent (especially with light gases and at higher temperatures) would result in more preferable dynamic adsorption parameters for the gases in the Jado LD 1191 beds.

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