Adiabatic adsorption of carbon dioxide in fixed bed of the molecular sieve Calsit 5

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The described model of adiabatic equilibrium adsorption is applied to the adsorption of carbon dioxide. The course of adsorptive concentration at the exit from adsorber calculated numerically and the course of temperature at selected spots of the layer of adsorbent are compared with the corresponding relationships found experimentally.

Была описана модель адиабатической равновесной адсорбции, которая использовалась для случая адсорбции двуокиси углерода. Сравниваются расчетные и экспериментально найденные значения концентрации адсорбтива при выходе из адсорбера и также температуры на отдельных высотах слоя адсорбента.

In literature, there are substantially less papers dealing with adiabatic adsorption than with isothermal adsorption. It is evidently due to the fact that the inclusion of heat balance into the equations describing the adsorption process in static layer of adsorbent gives a system of differential equations which is not analytically solvable in general case. The studies published are either based on the relatively rough simplification that the temperature and concentration profile does not change during the passage through the bed or are limited to the description of an adsorption system by partial differential equations which are to be solved numerically for the conditions of experiment. The latter procedure is characteristic of present publications.

Concise survey of the papers published

Todes and *Lezin* [1] derived relationships for the calculation of the rate of propagation of the concentration and heat wave from the differential equations describing the course of adiabatic equilibrium adsorption with infinitely rapid heat transfer in adsorption system for constant rate of propagation of the concentration and temperature profile through the layer of adsorbent. In this approach, they distinguish two cases. In the first case, the speed of the heat wave is greater than the speed of the sorption wave. In the second case, the speed of the isothermal sorption wave is greater than the speed of the heat wave. In paper [2], *Acrivos* applied the method of characteristics as a method of numerical solution of the partial differential equations describing adiabatic adsorption. *Leavitt* [3] put forward the analysis based on the idea of a stable zone of mass transfer. On the basis of the assumption of a stable zone of mass transfer and heat balance, he has postulated existence of two zones of mass transfer which, according to the author, arise in an adsorber of sufficient length provided the diameter of adsorber ensures that the portion of heat loss through the wall of adsorber has only small influence on mean temperature of the layer of adsorbent. *Meyer* and *Weber* [4] do not recommend to use the Leavitt relationships for calculating the length of the mass transfer zone because it is assumed in the derivation of these relationships that the speed of gas in the zone is constant. These authors have described the adsorption system by differential equations of mass and heat balance and taken into account the heat losses from the adsorber to the surroundings. They express the rate of mass transfer in the liquid phase by means of the convective mass transfer coefficient and in the solid phase by means of the diffusion coefficient. They described the adsorption equilibrium by the Peterson—Redlich equation and numerically solved the system of differential equations for the adsorption of methane on activated carbon from a flow of helium. The results obtained are in better conformity with particular temperatures in the adsorber than with verification of the break-through curve. The authors state that the model is very general but the calculation according to this model is very expensive. When the adsorber was divided into 16 increments, the calculation on IBM 7044 took two hours. *Amundson, Aris,* and *Swanson* [5] put forward a method of the solution of adiabatic equilibrium adsorption by means of dimensionless characteristics. A more detailed analysis of adiabatic adsorption based on the Leavitt postulation of two zones is presented in [6]. In that paper, *Pan* and *Basmadjian* formulated presumptions for two stable zones. The authors verified the derived relations by means of the experimental results obtained by investigating adsorption of carbon dioxide on the molecular sieve 5A which were published by *Leavitt* [3]. The results are in relatively good agreement for the first zone and for the equilibrium interzone of mass transfer. However, the agreement is not satisfactory for the second zone of mass transfer. *Zolotarev* and *Radushkevich* [7] analytically solved the equations decribing adiabatic adsorption in a separate spherical or cylindrical particle of adsorbent. *Rhee* and *Amundson* [8] theoretically analyzed the equilibrium multicomponent adiabatic adsorption with infinitely rapid heat transfer in an adsorber with countercurrent flow of phases. *Pan* and *Basmadjian* [9, 10] present an analysis of adiabatic equilibrium adsorption. In their studies, they use a modified procedure of *Amundson, Aris,* and *Swanson* published in [5]. *Carter* and *Husain* [11] allege a relatively good agreement of the experimental break-through curve of carbon dioxide on molecular sieve with the curve calculated from the isothermal model including the mass transfer resistance in the solid and liquid phase. They describe adsorption equilibrium by the Langmuir equation. The authors also describe the adsorption process of carbon dioxide and water on a layer of the molecular sieve 4A [12] by isothermal model and state a good agreement of the experimental break-through curve with the calculated curve in spite of the fact that the isothermal adsorption of water and carbon dioxide cannot be expected for the used adsorber having the diameter of 5.1 cm. *Zubov et al.* [13] investigated adiabatic adsorption of carbon dioxide on the molecular sieve 10X with different initial temperatures of adsorbent and found different rates of propagation of the temperature and concentration wave. The authors stated good agreement in relation of experimental results with the one heat wave theory according to Pan and Basmadjian for the region of low initial temperatures of the adsorbent layer. On the other hand, they found great differences at high initial temperatures of the adsorbent. *Cabek* [14] numerically solved the case of adiabatic adsorption of three components in a static layer of adsorbent. In his study he used the solution of propagating stationary wave which physically corresponded to constant rate of travel of the unchanging zone of mass transfer. *Cooney* [15] numerically solved the course of adiabatic adsorption of one component. In the calculation, he assumed an equilibrium in the form consistent with the Langmuir isotherm with one constant which depended on temperature according to the Clausius—Clapeyron equation. From the results obtained with the values of physical constants arbitrarily chosen, he stated the conditions for which the equilibrium adsorption could be assumed and which should be necessary for the formation of mesozone, *etc.* The published numerical solutions of adiabatic adsorption solve only certain real cases of adsorption. Therefore their use for the verification of experimental results and design of adsorber is limited because a new solution has to be found according to the model chosen for every real case.

In this paper the adiabatic course of adsorption of carbon dioxide is described by differential mass and heat balance. The differential equations describing the course of adsorption thus simplified as well as the modified equilibrium relationship are solved numerically. This physical model of adsorption corresponds to the thermodynamically maximum separation effect of adsorber and is a convenient comparative model for estimating the separation in real systems.

Mathematical description of adiabatic equilibrium adsorption

The adsorption in static layer of granulated adsorbent is a complicated process governed by the laws of hydrodynamics, mass and heat transport in the gaseous and solid phase, adsorption equilibrium and heat effects accompanying the adsorption on solid surface. The mathematical description of the course of adsorption is based on the following simplifying assumptions:

a) Only one substance is adsorbed from the stream of indifferent gas.

b) Physical characteristics of gas and solid material are constant and independent of temperature.

c) Gas flow is piston-like.

d) Owing to negligible amount of the component adsorbed, the flow rate may be regarded as constant.

e) The concentration of adsorptive and temperatures in both phases are explicit functions of the space and time and do not depend on radial position of the particle in the layer of adsorbent.

f) Both liquid and solid phases are considered to be continua existing in continuous contact beside each other in the interface the surface of which corresponding to a volume unit of the layer is definite.

g) The cross-section of the adsorber is constant.

h) The voidage fraction is constant.

The assumption of the piston-like flow of gas eliminates the transport of adsorptive by longitudinal diffusion.

Let us consider a volume element of the adsorber of the cross-section A and height dz shown in Fig. 1. The gas enters a volume element and gets out of it with the superficial velocity w. The values of adsorptive concentration and temperature at the entrance and exit from a volume element of the adsorber at the time τ are given in Fig. 1. The application of the law of conservation to the amount of adsorptive in a volume element gives the mass balance in the form

$$w\left(\frac{\partial c}{\partial z}\right)_\tau + \varepsilon\left(\frac{\partial c}{\partial \tau}\right)_z + \varrho_b\left(\frac{\partial a}{\partial \tau}\right)_z = 0 \tag{1}$$

where z, ε, ϱ_b, and a are coordinate of position along the bed, voidage fraction, bulk density of bed, and concentration of adsorbate in adsorbent in moles of adsorptive per kg of adsorbent, respectively.

If we assume that the heat loss to the surroundings is zero and apply the law of conservation to a volume element of the adsorber, the following equation of heat balance is to be derived

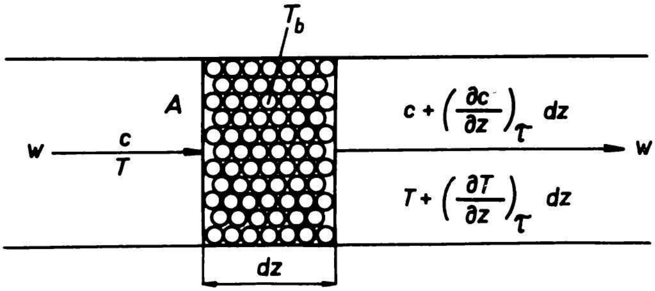

Fig. 1. Volume element of the bed.

$$w\left(\frac{\partial T}{\partial z}\right)_\tau + \varepsilon\left(\frac{\partial T}{\partial \tau}\right)_z + \frac{\varrho_b c_{pb}}{\varrho c_p}\left(\frac{\partial T_b}{\partial \tau}\right)_z - \frac{\varrho_b(-\Delta H)}{\varrho c_p}\left(\frac{\partial a}{\partial \tau}\right)_z = 0 \tag{2}$$

where c_p, c_{pb}, ϱ, T_b, and ΔH are mean heat capacity of gas, mean heat capacity of adsorbent, gas density, temperature of adsorbent, and enthalpy change during adsorption, respectively.

We shall assume that the equilibrium in the investigated system may be described by the following equation

$$a^* = A \exp(-BT_b)c^* \tag{3}$$

where A and B are constants. For solving eqns (*1—3*), the kinetic relations for mass and heat transfer and the initial and boundary conditions must be formulated. Assuming the adiabatic equilibrium adsorption with infinitely rapid heat transfer, it may be written $a^* = a$, $c^* = c$, and $T_b = T$ By introducing the parameters

$$W = \frac{w}{\varepsilon}, \quad D = \frac{\varrho_b}{\varepsilon}, \quad E = \frac{\varrho_b(-\Delta H)}{\varrho c_p \varepsilon}, \quad F = \frac{\varrho_b c_{pb}}{\varrho c_p \varepsilon} \tag{4}$$

eqns (*1*) and (*2*) may be rearranged into the form

$$\left(\frac{\partial c}{\partial \tau}\right)_z + W\left(\frac{\partial c}{\partial z}\right)_\tau + D\left(\frac{\partial a}{\partial \tau}\right)_z = 0 \tag{5}$$

$$\left(\frac{\partial T}{\partial \tau}\right)_z (1+F) + W\left(\frac{\partial T}{\partial z}\right)_\tau - E\left(\frac{\partial a}{\partial \tau}\right)_z = 0 \tag{6}$$

Hence, the equation of equilibrium line gives

$$\left(\frac{\partial a}{\partial \tau}\right)_z = A \exp(-BT)\left(\frac{\partial c}{\partial \tau}\right)_z - AB \exp(-BT)c\left(\frac{\partial T}{\partial \tau}\right)_z \tag{7}$$

For the adsorption on pure adsorbent at the temperature of adsorbent and entering gas T_0 and at the concentration of adsorptive in feed c_0, the initial and boundary conditions may be formulated as follows

$$\begin{aligned} &c(0, z) = 0, \quad T(0, z) = T_0, \quad a(0, z) = 0, \qquad \text{for } 0 \leqq z \leqq z_0 \\ &c(\tau, 0) = c_0, \quad T(\tau, 0) = T_0 \qquad \text{for } \tau > 0 \end{aligned} \tag{8}$$

The course of equilibrium adiabatic desorption with infinitely rapid heat transfer and equilibrium relation (*3*) is also described by eqns (*5—7*). However, the initial and boundary conditions must be changed. Provided the layer of adsorbent of the temperature T_0 is uniformly saturated to the value a_0 before desorption and is desorbed by the stream of an indifferent gas of the temperature T_0 which does not contain any adsorptive, the initial and boundary conditions may be formulated as follows

$$\begin{aligned} &c(0, z)=c_0, \quad T(0, z)=T_0, \quad a(0, z)=a_0 \qquad \text{for } 0 \leqq z \leqq z_0 \\ &c(\tau, 0)=0, \quad T(\tau, 0)=T_0 \qquad \text{for } \tau>0 \end{aligned} \tag{9}$$

where c_0 is the equilibrium concentration in gas corresponding to the concentration in adsorbent a_0 at the temperature T_0.

Verification of the adiabatic equilibrium model

The system of partial differential eqns (*5*—*7*) with initial and boundary conditions (*8*) was numerically solved for the adsorption of carbon dioxide on the molecular sieve Calsit 5 from a stream of nitrogen. In this calculation, the values of physical quantities corresponding to experiment were used, *i.e.* length of the bed $z_0 = 0.66$ m, inside diameter of the adsorber 39 mm, Calsit 5 balls ϕ 2—3 mm, temperature of the entering gas and initial temperature of the bed $T_0 = 298$ K, concentration of adsorptive in the entering gas $c_0 = 8.156$ mol m^{-3}, the modified Reynolds number 18, $W = 1125.4$ m h^{-1}, $D = 1933.1$ kg m^{-3}, $F = 2237.4$ including the heat capacity of the adsorber, and $E = 73835.3$ K kg mol^{-1} The values of the constants A and B in eqn (*3*) were calculated from the equilibrium data of the adsorption of carbon dioxide on molecular sieve published in [16], *i.e.* $A = 0.766$ m^3 kg^{-1} and $B = 3.0 \times 10^{-3}$ K^{-1} The calculations were carried out on a computer Siemens 4004/150 in the programming language SIKOS. The calculation with the error corresponding to 2% of the bed length did not last more than 5 min. The results of calculations as well as the experimental relationships are represented in Figs. 2 and 3. Fig. 2 shows that the break point times corresponding

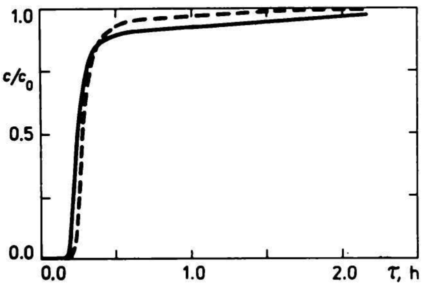

Fig. 2. c/c_0 as a function of time for $Re = 18$.
— — — Calculated; ——— experimental.

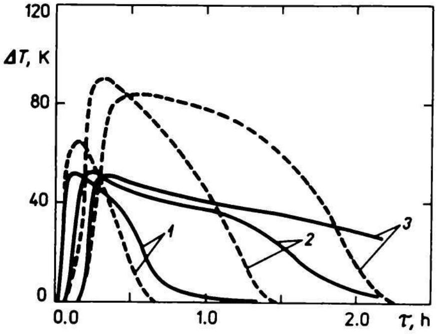

Fig. 3. Temperature in the bed as a function of time for $Re = 18$.
— — — Calculated; ——— experimental.
1. 136 mm; *2.* 405 mm; *3.* 657 mm from the inlet to the bed.

to the experimental and calculated curve hardly differ from each other. However, the character of the calculated break-through curve does not correspond to the character of the experimental curve. The differences between both curves are evidently due to the limitations resulting from the idea of adiabatic equilibrium adsorption and the postulate of linear form of the adsorption isotherm.

It is obvious from Fig. 3 that the time courses of temperature corresponding to each other in arbitrary spots of the adsorber differ almost by 100%. As the pertinent thermocouple measured temperature of the glass wall in the port connection of the adsorber, the measured values of temperature are lower than the real values. The differences between the calculated and real temperatures are, therefore, smaller than the differences represented in Fig. 3. The errors due to temperature measurements do not exceed the range of a decimal order while the differences between corresponding temperatures in Fig. 3 are higher by one decimal order. The differences between corresponding temperatures as well as the difference in the form of the break-through curves are related to the simplifications used in the derivation of the calculating procedure.

Conclusion

The break-through curve found experimentally is deformed in the region of higher concentrations. However, the formation of the second zone of mass transfer described in literature was not observed. The break point times of the experimental curve and of the curve calculated from the idea of adiabatic equilibrium adsorption with the equilibrium described by eqn (*3*) are relatively in good agreement. In lack of kinetic data, the model of adiabatic equilibrium adsorption may be used for calculating the break point time in the investigated adsorption system or in physically similar systems.

Symbols

a	concentration of adsorbate in adsorbent	mol kg^{-1}
a^*	equilibrium concentration of adsorbate in adsorbent	mol kg^{-1}
A	cross-section of the adsorber	m^2
A	constant in eqn (*3*)	m^3 kg^{-1}
B	constant in eqn (*3*)	K^{-1}
c	concentration of adsorptive in the fluid phase	mol m^{-3}
c^*	equilibrium concentration of adsorptive in the fluid phase	mol m^{-3}
c_0	concentration of adsorptive in the feed	mol m^{-3}
c_p	mean heat capacity of the fluid phase	J kg^{-1} K^{-1}
c_{pb}	mean heat capacity of adsorbent	J kg^{-1} K^{-1}
D	parameter defined by eqn (*4*)	kg m^{-3}

E	parameter defined by eqn (*4*)	K kg mol^{-1}
F	parameter defined by eqn (*4*)	—
ΔH	enthalpy change accompanying adsorption	J mol^{-1}
T	temperature of the fluid phase	K
T_b	temperature of adsorbent	K
T_0	initial temperature of the bed and temperature of the feed	K
w	superficial gas velocity	m s^{-1}
W	interstitial gas velocity	m s^{-1}
z	length of the bed	m
ε	voidage fraction	—
ϱ	density of the fluid phase	kg m^{-3}
ϱ_b	bulk density of the bed	kg m^{-3}
τ	time	s

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