Adiabatic equilibrium desorption of carbon dioxide from molecular sieve fixed bed by the stream of inert gas

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A proposed model of adiabatic equilibrium desorption is applied to the desorption of carbon dioxide from a bed of granulated molecular sieve into the stream of inert gas. The course of temperature along the hight of adsorbent bed and the course of adsorptive concentration in the stream of desorbent at the exit from the adsorber have been calculated numerically and compared with the relations obtained experimentally in an equipment of laboratory dimensions.

Предложена модель адиабатической равновесной десорбции, которая применена к случаю десорбции CO_2 из слоя гранулированного молекулярного сита током инертного газа. Численно рассчитанный ход температур в избранных слоях адсорбента и концентрационной зависимости адсорбтива в токе десорбента на выходе адсорбера сравнивается с зависимостями, обнаруженными экспериментально на аппарате лабораторного масштаба.

The industrial separation of gaseous mixture by adsorption is at present almost exclusively performed in fixed bed adsorbers in a cyclic process where the period of adsorption alternates with the period of desorption. The continuity of the process is attained by a system of several adsorbers the number of which depends on the ratio of the periods of time necessary for adsorption and desorption with respect to an eventual adjustment of the bed of adsorbent before the period of adsorption. The time necessary for desorption itself and the time necessary for the adjustment of the bed of adsorbent usually exceeds the period of adsorption and consequently, the number of adsorbers in the system depends on the rate of desorption. As the desorption commonly demands more energy than the adsorption, the technical and economic indices of desorption predetermine the investment and operation expences of separation and thus its economic effectivity. In spite of this fact, the literature dealing with the theoretical and practical problems concerning the realization of desorption is rather poorer in information than the literature dealing with the adsorption itself. In principle, the desorption in systems of this kind may be realized by exhausting the adsorbate from the bed of adsorbent and thus reducing the total pressure, by the flow of inert gas which ensures the depression of partial pressure of adsorptive over the interface or by stripping the adsorbate from

the adsorbent by a substance which is more easily adsorbed. Each of these procedures may be intensified by raising the temperature of the bed by heat input which can be performed either by indirect heating or by direct heating using the inert gas as a heat carrier. From the practical point of view, the simplest method of desorption is the desorption by inert gas in connection with the supply of heat.

Review of the published papers

An exact solution providing a method for calculating such fundamental chemical engineering data as the time of desorption period, the consumption of heat and inert gas at simultaneous heat supply has not been presented yet. The papers published can be divided into two groups. The analysis of desorption conceived as an isothermal process is characteristic of the first group [1—3]. Owing to the endothermic character of desorption, these papers are more of theoretical than practical importance. From the practical view-point, the papers analyzing the desorption by inert gas as an adiabatic process are more important. *Amundson* [4] was the first to put forward a mathematical model of adiabatic equilibrium desorption. This model was modified by *Pan* and *Basmadjian* [5] and subsequently improved by introducing a nonlinear relation for expressing the adsorption isotherm of the so-called favourable form [6]. According to [7], the temperature and concentration profiles in the bed of adsorbent thus calculated were consistent with the experimental data in a measure allowing a realistic estimate of characteristic operational parameters for desorption. *Carter* [8] published a model of nonisothermal desorption with prevailing resistance in the stream of desorbent and used a nonlinear relationship for adsorption isotherm. The contribution of this solution is not great when compared with the solution for equilibrium desorption because, if some influence of the kinetics of substance transport on the course of desorption is expected, it may be rightly assumed that this influence must result from the resistance against the substance transport in particle of adsorbent. The model of nonisothermal desorption of water from silica gel published by *Lychkin et al.* [9] cannot be regarded as a calculational procedure for designing the desorption stage of the process of separation because it is founded on the known experimental temperature profiles in the bed of adsorbent.

The references to the published papers show that the attention to the problems of adiabatic desorption was paid merely in recent years and therefore the amount of information available is rather poor. In this paper, we consider the applicability of the model of adiabatic equilibrium desorption proposed by us [10] for the description of adiabatic equilibrium desorption of carbon dioxide from a fixed bed of molecular sieve by the stream of nitrogen. Though this model represents a considerable simplification in view of the processes taking place under real conditions in general, it is a foundation on which we may formulate more

sophisticated model ideas involving the effects of superimposed processes which can be assumed to be of importance under real conditions. Moreover, this model may be used as a reference model for quantification of the mentioned effects.

Mathematical description of adiabatic equilibrium desorption

In general, the desorption of substance from an adsorbent bed by the stream of indifferent gas is a complex process characterized by unsteady transfer of substance and heat. The presented mathematical description is related to a simplified physical model based on the following assumptions:

a) The adsorbate is desorbed from an adsorbent bed by the stream of indifferent gas the inlet temperature of which is constant.

b) The physicochemical characteristics of indifferent gas, adsorptive, and solid material are constant and independent of temperature.

c) The flow of gas is piston-like.

d) Because of a low concentration of adsorptive, the flow rate of gas in the adsorber may be considered constant.

e) The concentrations of adsorptive and temperature in both phases are one-valued functions of position and time and are independent of the radial coordinate.

f) Both phases, *i.e.* fluid and solid, are regarded as continua existing next to each other in a continuous contact on the interface the surface area of which related to a volume unit of the bed is definite.

g) The voidage fraction and cross-section of adsorber are constant.

The course of substance desorption from adsorbent in a fixed bed arrangement by the stream of inert gas under the above simplifying assumptions can be described by the equations of differential substance balance [10]

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

and differential heat balance

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

We shall assume that the equilibrium in the investigated system may be described by the modified Henry relationship in the form

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

The assumption of the adiabatic equilibrium desorption leads to the following relationships between concentrations and temperatures

$$a^* = a, \quad c^* = c, \quad T_b = T \tag{4}$$

On inserting expressions (4), eqns (1—3) may be solved for convenient initial and boundary conditions.

If a layer of adsorbent of the temperature T_0 which is uniformly saturated to the value a_0 is desorbed by the stream of indifferent gas of the temperature T_0 which does not contain any adsorptive, the initial and boundary conditions may be formulated as follows [10]

$$c(0, z) = c_0, \quad T(0, z) = T_0, \quad a(0, z) = a_0 \qquad \text{for } 0 \leqslant z \leqslant z_0$$
$$c(\tau, 0) = 0, \quad T(\tau, 0) = T_0 \qquad \text{for } \tau > 0 \tag{5}$$

Eqns (1—4) were solved for conditions (5) by simulation on a digital computer Siemens 4004/150. On introducing the parameters

$$W = \frac{w}{\varepsilon}, \quad D = \frac{\varrho_b}{\varepsilon}, \quad E = \frac{\varrho_b(-\Delta H)}{\varrho c_p \varepsilon}, \quad F = \frac{\varrho_b c_{pb}}{\varrho c_p \varepsilon} \tag{6}$$

with respect to the fact that $F \gg 1$ and $DA \exp(-BT) \gg 1$, the system of eqns (1—4) has been rearranged into the following two equations

$$\left(\frac{\partial c}{\partial \tau}\right)_z = -\frac{W[F + ABEc \exp(-BT)]}{ADF \exp(-BT)} \left(\frac{\partial c}{\partial z}\right)_\tau - \frac{BcW}{F} \left(\frac{\partial T}{\partial z}\right)_\tau \tag{7}$$

$$\left(\frac{\partial T}{\partial \tau}\right)_z = -\frac{EW}{DF} \left(\frac{\partial c}{\partial z}\right)_\tau - \frac{W}{F} \left(\frac{\partial T}{\partial z}\right)_\tau \tag{8}$$

Verification of the adiabatic equilibrium model of desorption

In order to compare the results obtained by solving the theoretical model, the experimental results obtained in the experiment characterized by subsequent data are given.

The bed of the molecular sieve Calsit 5 containing pellets of 2—3 mm in diameter was uniformly saturated with carbon dioxide which was adsorbed from the stream of nitrogen at 298 K. The inlet concentration of CO_2 was 7.48 mol m^{-3} during adsorption. According to eqn (3), the equilibrium concentration 2.34 moles of CO_2 per 1 kg of adsorbent corresponded to the above value of inlet concentration of CO_2.

Carbon dioxide was desorbed by the stream of nitrogen (0.196 m^3 h^{-1}, 298 K, pressure 103.99 kPa at the inlet into the adsorber) from the adsorbent prepared in such way (length of bed 0.66 m, diameter 0.039 m, and voidage fraction $\varepsilon = 0.373$). The experimental conditions were chosen with respect to the subsequent demands. The temperature of the desorption agent (nitrogen) at the inlet into the adsorber should be equal to the temperature of the bed of adsorbent after finishing its saturation in the stage of adsorption. The high initial concentration of adsorbate on adsorbent was so chosen that the effect of the heat of desorption should

manifest itself as a factor markedly distinguishing the course of the process under adiabatic conditions from its course under isothermal conditions. The value of the flow rate of nitrogen was so chosen that the influence of the resistance against the transfer of substance and heat in the flow of desorbent should be suppressed by turbulence of the flow ($Re = 8$).

The above experimental conditions give the following values of the parameters used for solving eqns (7) and (8): $W = 500.24$ m h^{-1}, $D = 1933.1$ kg m^{-3}, $E = 73\,835.3$ kg K mol^{-1}, $F = 2237.4$.

In contrast to the definition given by eqn (6), the value of parameter F includes the heat capacity of the adsorber body, which results in the following expression

$$F = \frac{\varrho_b c_{pb} + \left(\dfrac{S_1}{A_1}\right)\varrho_s c_{ps}}{\varrho c_p \varepsilon} \tag{9}$$

The values of constants A and B in eqn (3) were taken from paper [10].

The calculated and experimental results are illustrated in Figs. 1 and 2.

Fig. 1. Dependences of c/c_0 on time at $Re = 8$.
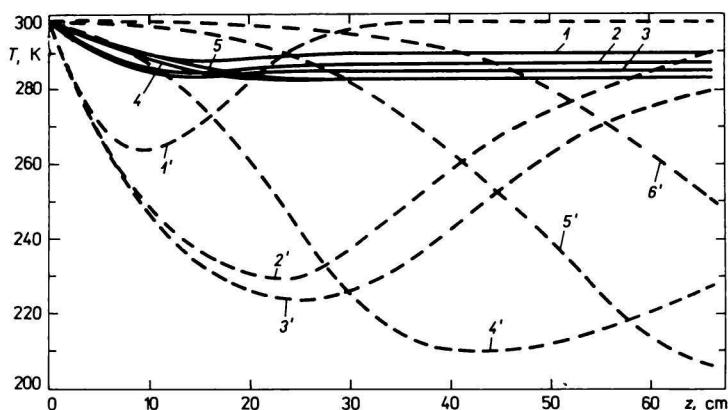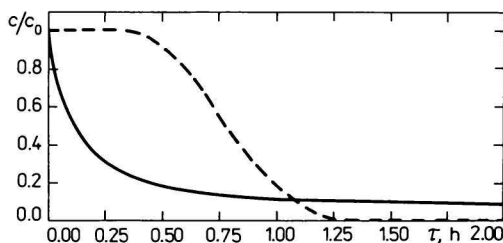— — — Calculated; ——— experimental.

Fig. 2. Temperature course in the adsorber at particular time intervals after the start of desorption.
— — — — Calculated according to the model; ——— experimental.
1., 1'. 0.1 h; 2., 2'. 0.4 h; 3., 3'. 0.5 h; 4., 4'. 1 h; 5., 5'. 2 h; 6'. 3 h.

Fig. 1 represents the time dependence of the dimensionless concentration of adsorptive in the outlet stream from the adsorber. The dimensionless concentration of CO_2 is defined as the ratio of its concentration in the stream of nitrogen to the equilibrium concentration corresponding to saturation of the adsorbent before the start of desorption. Analogous relationships at particular distances along the length of the adsorbent bed are not plotted because the calculated values cannot be compared with the experimental ones. The experimental apparatus did not allow to measure the concentration of CO_2 in the stream of nitrogen at particular distances from the inlet into the adsorber.

Fig. 2 represents the course of temperature along the length of the adsorbent bed. The parameter is the time of desorption. The experimental curves are drawn through the points corresponding to the values of gas temperature measured on six spots along the length of the bed. The curves drawn through the calculated values give the temperatures of gas and adsorbent which, in conformity with the physical model, must be equal.

Discussion

The form of the curve expressing the calculated concentration of CO_2 in nitrogen at the outlet from the adsorber as a function of time (Fig. 1) indicates a zonal character of the course of desorption. The same conclusion can be also drawn from the analysis of the calculated temperature relationships (Fig. 2). Neither of these relationships confirms the formation of two zones for the particular conditions of process described in literature [7].

The shape of the break-through curve found experimentally (Fig. 1), however, does not imply the zonal character of desorption and the experimental temperature relationships do not confirm this character either (Fig. 2). We cannot infer from these results whether the zone expected according to the theory of adiabatic equilibrium desorption was not formed only because the length of experimental layer of adsorbent was not satisfactory for the development of this zone because of a small rate of the transfer of heat and substance between gas and particles and in the particles themselves or whether the desorption proceeded during the process more or less uniformly within the whole length of layer. The second idea is more consistent with the experimental temperature relationships which show a slight fall at every time of desorption and almost an isothermal course along the length of layer except a small section at the inlet into the adsorber. In respect of the fact that the temperature was measured by thermocouples inserted into punctures in the glass wall of the adsorber, the real temperature of gas was lower than the reading of thermocouples. Nevertheless, this difference between the measured and real temperature of gas cannot exceed a few degrees and substantially distort the above idea.

The calculated courses of temperature reveal that a considerable decrease in temperature of adsorbate on adsorbent appears during desorption. It is possible to obtain more accurate values of these theoretically calculated temperatures by expressing the equilibrium relationships by a more adequate form correlating the equilibrium at very low temperatures. The values of constants A and B in eqn (3) were calculated from the equilibrium data of the adsorption of carbon dioxide on molecular sieve at temperatures which might occur during adsorption, *i.e.* 298—333 K. In spite of the inaccuracy due to the extrapolation of this relationship to much lower temperatures, the minimum of the calculated temperature functions varies in the region corresponding to the freezing point of carbon dioxide. As the real rate of desorption possesses a finite value, the temperature of adsorbent is higher than the calculated value. The low heat conductivity of a particle of adsorbent and of a crystal of molecular sieve, however, indicates that the real temperature of a crystal of molecular sieve must be low enough for assuming a change in state behaviour of the adsorbed phase under given conditions of desorption. The change in state of the adsorbed phase considerably reduces the rate of desorption. However, it can also produce a change in the character of desorption.

Therefore, the conditions of desorption must be so chosen that this state does not occur during desorption. An increase in flow rate of the desorbent with the same specific enthalpy does not have to improve the conditions. The desorbent gives up the apparent heat almost exclusively to the surface of adsorbent particle and not to the crystal of zeolite. Therefore, if we want to convey the apparent heat of desorbent as far as the adsorbed phase in a crystal of zeolite and thus to prevent a change in state of the adsorbed phase, we must raise the driving force of heat transfer by raising the temperature of desorbent. A decrease in the flow rate of desorbent results in a decrease in the rate of desorption and thus in a decrease in undercooling of the adsorbed phase. However, that need not be technologically interesting because the total amount desorbed in the limited time interval is small at low flow rates of desorbent. A change in state of the adsorbed phase may be also so prevented that a sufficiently high initial temperature of adsorbent and desorption medium is used.

Conclusion

The proposed model of adiabatic equilibrium desorption is not adequate to describe the desorption of carbon dioxide from a fixed bed of molecular sieve by the stream of nitrogen under given conditions.

The confrontation of calculated and experimental results enables us to conclude that the practical realization of the desorption of carbon dioxide from molecular sieve necessitates a sufficiently high specific enthalpy of the desorption gas. As the specific heats of the gases coming into consideration as desorbents are not very

different, an increase in enthalpy of the desorbent may be achieved only by increasing its temperature at the inlet into the adsorber.

The proposed model of adiabatic equilibrium desorption must be verified under such conditions when no change in state of the adsorbed phase occurs during desorption.

Symbols

a	adsorbate concentration	$mol\ kg^{-1}$
$a*$	equilibrium adsorbate concentration	$mol\ kg^{-1}$
A	constant in eqn (3)	$m^3\ kg^{-1}$
A_1	cross-section of the adsorber	m^2
B	constant in eqn (3)	K^{-1}
c	concentration of adsorptive in fluid phase	$mol\ m^{-3}$
$c*$	equilibrium adsorptive concentration 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	$J\ kg^{-1}\ K^{-1}$
c_{ps}	mean heat capacity of glass	$J\ kg^{-1}\ K^{-1}$
D	parameter defined by eqn (6)	$kg\ m^{-3}$
E	parameter defined by eqn (6)	$kg\ K\ mol^{-1}$
F	parameter defined by eqn (6)	—
ΔH	enthalpy change accompanying adsorption	$J\ mol^{-1}$
S_1	cross-section area of the wall of adsorber	m^2
T	temperature of the fluid phase	K
T_b	temperature of adsorbent	K
T_0	initial temperature of the bed and the inlet stream temperature	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 adsorbent	$kg\ m^{-3}$
ϱ_s	density of glass	$kg\ m^{-3}$
τ	time	s

References

1. Zwiebel, I. and Schnitzer, J. J., *AIChE Symp. Ser. 134,* 18 (1974).
2. Seballo, A. A., Lezin, Yu. S., Plachenov, T. G., and Baranov, E. I., *Zh. Fiz. Khim. 48,* 1202 (1974).
3. Keľtsev, N. V., *Gaz. Prom. 9,* 51 (1964).
4. Amundson, N. R., Aris, R., and Swanson, P., *Proc. Roy. Soc. A286,* 129 (1965).
5. Pan, C. Y. and Basmadjian, D., *Chem. Eng. Sci. 26,* 45 (1971).
6. Basmadjian, D., Ha, K. D., and Pan, C. Y., *Ind. Eng. Chem., Process Des. Develop. 14,* 328 (1975).

7. Basmadjian, D., Ha, K. D., and Proulx, D. P., *Ind. Eng. Chem., Process Des. Develop.* **14,** 340 (1975).
8. Carter, J. W., *AIChE J.* **21,** 380 (1975).
9. Lychkin, I. P., Rizov, Z. M., and Todes, O. M., *Zh. Prikl. Khim.* **4,** 1225 (1961).
10. Bobok, D., Kossaczký, E., and Báleš, V., *Chem. Zvesti* **33**, 357 (1979).

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