

PERIODIC STEADY-STATE SOLUTION TO PRESSURE SWING ADSORPTION WITH SHORT CYCLE TIME

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A set of differential equations describing the material balance of PSA operated at periodic steady state was expanded into a power series of small value of $\lambda (=K_A a t_c / \rho_s)$ and the following solution was derived for the average concentration of product $\overline{C_{A1}}$ and its swing ΔC_{A1} .

$$\overline{C_{A1}} = C_{A1}^{(0)}(1 + \lambda^2 H^{(2)}), \quad \Delta C_{A1} = \lambda C_{A1}^{(0)} M^{(1)}$$

in which

$$C_{A1}^{(0)} = (1 - \eta) / (1 - \eta p_D / p_A), \quad \eta = (1 - E_1) / (1 - E_1 u_A / u_D)$$

$$M^{(1)} = (1 - p_D / p_A)(1 - E_2) / (K_A / K_D + u_A / u_D)$$

$$\ln E_1 = -(K_A a m L / u_A)(1 - u_A / u_D) / (1 + K_A / K_D)$$

$$\ln E_2 = -(K_A a m L / u_A)(K_A / K_D + u_A / u_D) / (1 + K_A / K_D)$$

and $H^{(2)}$ is a function given in the text. Parameters $K_A a$, L , m , p , u and ρ_s , respectively, are overall volumetric mass transfer coefficient, column length, adsorption coefficient, pressure, superficial gas velocity and bulk density. Subscripts A and D , respectively, refer to adsorption and desorption steps. The present analysis holds when $\lambda < 2$ and the term $\lambda^2 H^{(2)}$ can be neglected when $\lambda < 0.5$.

Introduction

Pressure swing adsorption (PSA) has gained increasing interest in commercial application to gas separation. Many variables are coupled complicatedly in a PSA system and thus the prediction of performance cannot be made straightforwardly even when the system is restricted to gas purification in which a trace of a single adsorbate is removed from non-adsorbable carrier gas. Earlier equilibrium theory has been followed by a recent analysis based on a dynamic model, which is more realistic in that the finite rate of mass transfer is taken into account to predict the profiles of the adsorbate concentration and amount adsorbed. The recent development of the dynamic model for gas purification is as follows. Kawazoe and Kawai⁴ extended a breakthrough curve in fixed bed to interpret the PSA separation of ⁸⁵Kr from nitrogen. Mitchell and Shendalman⁵ and Carter and Wyszynski,¹ respectively, interpreted their experimental results for CO₂ removal from He and air drying by numerical simulation based on the dynamic model. Chihara and Suzuki^{2,3} solved numerically the governing differential equations for both isothermal and non-isothermal operations by the finite difference

method and discussed effects of various parameters on PSA performance. Suzuki⁷ has proposed a simplified model based on the analogy to countercurrent mass transfer. Raghavan, Hassan and Ruthven⁶ developed an orthogonal collocation method to save computation time and discussed the effect of axial dispersion of gas.

The present work is also concerned with simulation of PSA performance based on such a dynamic model as above^{2,3,6,7}, but three points should be mentioned. Firstly, all available analyses employ numerical methods, which can yield a solution for any set of parameters. However, they cannot give any guidance in correlating the effects of variables, while analytical solution automatically involves the interrelation between variables. In addition, an analytical solution is handier for the estimation of performance in practice. Thus the purpose of the present work is to propose an analytical solution to PSA performance in a simple form. Secondly, PSA operation finally reaches a periodic steady state after an oscillating transient period. The present work is, however, limited to the periodic steady state because it is more important in long-time operation in practice. Finally, the highest possible performance can be obtained when adsorption and desorption steps are alternately switched in a short cycle time for frequent regeneration of ad-

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sorbent. The present analysis covers in particular this high-performance operation.

1. Basic Equation and Its Expansion

Figure 1 shows schematically a dual-column adsorber in which each column is operated alternately in a high-pressure (adsorption) step and a low-pressure (desorption) step. This two-step mode of PSA is considered in this study because this mode is very fundamental in PSA and is mathematically simple. Other simplifications employed are: single-component adsorption of dilute adsorbate, linear isotherm, linear driving force with constant mass transfer coefficient, plug flow of gas with constant superficial velocities and isothermal operation.

The basic material balance is formulated in terms of nomenclature shown in Fig. 1 as follows.

$$-u_A \frac{\partial c_A}{\partial x} - \varepsilon \frac{\partial c_A}{\partial t} = K_A a (m c_A - q_A) \quad (1)$$

$$\rho_s \frac{\partial q_A}{\partial t} = K_A a (m c_A - q_A) \quad (2)$$

for adsorption step ($0 \leq t \leq t_c$)

$$u_D \frac{\partial c_D}{\partial x} - \varepsilon \frac{\partial c_D}{\partial t} = K_D a (m c_D - q_D) \quad (3)$$

$$\rho_s \frac{\partial q_D}{\partial t} = K_D a (m c_D - q_D) \quad (4)$$

for desorption step ($t_c \leq t \leq 2t_c$)

The second term in Eqs. (1) and (3), $\varepsilon \partial c / \partial t$, is negligibly small relative to the first term since half-cycle time t_c is much greater than space time of gas (L/u). Thus, sufficient initial and boundary conditions for the periodic steady state lead to

$$c_A = c_{A0} \quad \text{at } x=0 \quad (5)$$

$$c_D|_t = (p_D/p_A) c_A|_{t-t_c} \quad \text{at } x=L \quad (6)$$

$$q_A = q_D \quad \text{at } t=t_c \quad (7)$$

$$q_A|_{t=0} = q_D|_{t=2t_c} \quad (8)$$

The initial condition Eq. (8) is equivalent to the equation

$$K_A \int_0^{t_c} (m c_A - q_A) dt + K_D \int_{t_c}^{2t_c} (m c_D - q_D) dt = 0 \quad (9)$$

which is obtained by summing Eqs. (2) and (4) after integration.

Basic equations and auxiliary conditions are rewritten into nondimensional form as

$$\partial C_A / \partial X = -N_A (C_A - Q_A) \quad (1')$$

$$\partial Q_A / \partial \tau = \lambda (C_A - Q_A) \quad (2')$$

$$\partial C_D / \partial X = \delta N_A (C_D - Q_D) \quad (3')$$

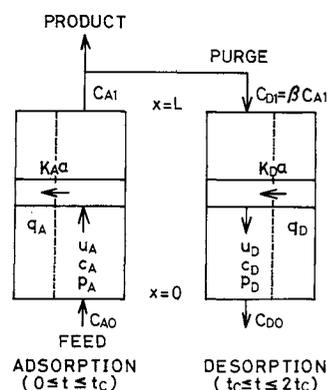


Fig. 1. Nomenclature for material balance.

$$\partial Q_D / \partial \tau = \gamma \delta \lambda (C_D - Q_D) \quad (4')$$

$$C_A = 1 \quad \text{at } X=0 \quad (5')$$

$$C_D|_{\tau} = \beta C_A|_{\tau-1} \quad \text{at } X=1 \quad (6')$$

$$Q_A = Q_D \quad \text{at } \tau=1 \quad (7')$$

$$\int_0^1 (C_A - Q_A) d\tau + \gamma \delta \int_1^2 (C_D - Q_D) d\tau = 0 \quad (9')$$

in terms of dimensionless variables defined by

$$C = c/c_{A0} \quad (10)$$

$$Q = q/mC_{A0} \quad (11)$$

$$\tau = t/t_c \quad (12)$$

$$X = x/L \quad (13)$$

$$N = KamL/u \quad (14)$$

$$\lambda = K_A a t_c / \rho_s \quad (15)$$

$$\beta = p_D/p_A \quad (16)$$

$$\gamma = u_D/u_A \quad (17)$$

$$\delta = N_D/N_A \quad (18)$$

The parameter λ can be written as $\lambda = K_A a m L c_{A0} t_c / m c_{A0} \rho_s L$, which is a characteristic ratio of cumulative amount adsorbed during half-cycle time relative to the maximum amount adsorbed when complete saturation is attained. Since the parameter λ is a small quantity in a short cycle time operation, a perturbation solution expanded around a small value of λ can be assumed as follows.

$$C = C^{(0)} + \lambda C^{(1)} + \lambda^2 C^{(2)} + \dots + \lambda^i C^{(i)} + \dots \quad (19)$$

$$Q = Q^{(0)} + \lambda Q^{(1)} + \lambda^2 Q^{(2)} + \dots + \lambda^i Q^{(i)} + \dots \quad (20)$$

When coefficients of like powers of λ are equated after substituting Eqs. (19) and (20) into Eqs. (1')–(9'), the basic equations and auxiliary conditions are expanded as follows for perturbed functions $C^{(i)}$ and $Q^{(i)}$:

$$\partial C_A^{(i)} / \partial X = -N_A (C_A^{(i)} - Q_A^{(i)}) \quad (1'')$$

$$\left. \begin{aligned} \partial Q_A^{(i)}/\partial \tau = 0 & \quad \text{for } i=0 \\ & = C_A^{(i-1)} - Q_A^{(i-1)} \quad \text{for } i \geq 1 \end{aligned} \right\} (2'')$$

$$\partial C_B^{(i)}/\partial X = \delta N_A (C_B^{(i)} - Q_B^{(i)}) \quad (3'')$$

$$\left. \begin{aligned} \partial Q_B^{(i)}/\partial \tau = 0 & \quad \text{for } i=0 \\ & = \gamma \delta (C_B^{(i-1)} - Q_B^{(i-1)}) \quad \text{for } i \geq 1 \end{aligned} \right\} (4'')$$

$$\left. \begin{aligned} C_A^{(i)} = 1 & \quad \text{at } X=1 \quad \text{for } i=0, \\ C_A^{(i)} = 0 & \quad \text{at } X=1 \quad \text{for } i \geq 1 \end{aligned} \right\} (5'')$$

$$C_B^{(i)}|_{\tau} = \beta C_A^{(i)}|_{\tau-1} \quad \text{at } X=1 \quad (6'')$$

$$Q_A^{(i)} = Q_B^{(i)} \quad \text{at } \tau=1 \quad (7'')$$

$$\int_0^1 (C_A^{(i)} - Q_A^{(i)}) d\tau + \gamma \delta \int_1^2 (C_B^{(i)} - Q_B^{(i)}) d\tau = 0 \quad (9'')$$

For the new set of equations, i.e. Eqs. (1'')–(9''), mathematical difficulties are greatly reduced compared to the original set, Eqs. (1')–(9').

2. Solution of Differential Equations

2.1 Solution of the zeroth-order term ($i=0$)

Functions $Q_A^{(0)}$ and $Q_B^{(0)}$ are found to be independent of time τ from Eqs. (2'') and (4''), and this fact implies that $C_A^{(0)}$ and $C_B^{(0)}$ are also independent of τ . Integration of Eq. (9'') yields

$$Q_A^{(0)} = Q_B^{(0)} = Q^{(0)} = (C_A^{(0)} + \gamma \delta C_B^{(0)}) / (1 + \gamma \delta) \quad (21)$$

and Eqs. (1'') and (3'') lead to

$$dC_A^{(0)}/dX = -N_A \{ \gamma \delta / (1 + \gamma \delta) \} (C_A^{(0)} - C_B^{(0)}) \quad (22)$$

$$dC_B^{(0)}/dX = -N_A \{ \delta / (1 + \gamma \delta) \} (C_A^{(0)} - C_B^{(0)}) \quad (23)$$

by substituting Eq. (21). Solution of the above equations satisfying boundary conditions can easily be obtained as

$$(1 - C_A^{(0)}) / (1 - C_A^{(0)}) = (1 - E_1^X) / (1 - E_1) \quad (24)$$

$$(1 - C_B^{(0)}) / (1 - C_A^{(0)}) = (1 - E_1^X / \gamma) / (1 - E_1) \quad (25)$$

$$(1 - Q^{(0)}) / (1 - C_A^{(0)}) = \left(1 - \frac{1 + \delta}{1 + \gamma \delta} E_1^X \right) / (1 - E_1) \quad (26)$$

In the above equations, $C_{A1}^{(0)}$ is the concentration of product gas and is given by

$$C_{A1}^{(0)} = (1 - \eta) / (1 - \beta \eta) \quad (27)$$

in which

$$\eta = \frac{(1 - E_1)}{(1 - E_1 / \gamma)} \quad (28)$$

and

$$\ln E_1 = -N_A \delta (\gamma - 1) / (1 + \gamma \delta) \quad (29)$$

2.2 Solution of the first-order term ($i=1$)

Substituting Eqs. (24)–(26) into Eqs. (2'') and (4'') and integrating them yield

$$Q_A^{(1)} = \kappa_1 \left(\tau - \frac{1}{2} \right) G_A^{(1)} + A^{(1)} \quad (30)$$

$$Q_B^{(1)} = -\kappa_1 \left(\tau - \frac{3}{2} \right) G_B^{(1)} + A^{(1)} \quad (31)$$

in which

$$\kappa_1 = C_{A1}^{(0)} \gamma \delta (1 - \beta) / (1 + \gamma \delta) E_1 \quad (32)$$

$$G_A^{(1)} = G_B^{(1)} = E_1^X \quad (33)$$

Thus, one may expect the following form of solution of $C_A^{(1)}$ and $C_B^{(1)}$:

$$C_A^{(1)} = \kappa_1 S_A^{(1)} \left(\tau - \frac{1}{2} \right) + B_A^{(1)} \quad (34)$$

$$C_B^{(1)} = -\kappa_1 S_B^{(1)} \left(\tau - \frac{3}{2} \right) + B_B^{(1)} \quad (35)$$

In Eqs. (30)–(35), functions $A^{(1)}$, $B_A^{(1)}$, $B_B^{(1)}$, $S_A^{(1)}$ and $S_B^{(1)}$ depend on X only and must be determined to satisfy the following equations:

$$dS_A^{(1)}/dX = -N_A (S_A^{(1)} - E_1^X) \quad (36)$$

$$dS_B^{(1)}/dX = \delta N_A (S_B^{(1)} - E_1^X) \quad (37)$$

$$dB_A^{(1)}/dX = -N_A (B_A^{(1)} - A^{(1)}) \quad (38)$$

$$dB_B^{(1)}/dX = \delta N_A (B_B^{(1)} - A^{(1)}) \quad (39)$$

$$B_A^{(1)} - A^{(1)} + \gamma \delta (B_B^{(1)} - A^{(1)}) = 0 \quad (40)$$

with boundary conditions

$$S_A^{(1)} = 0, \quad B_A^{(1)} = 0 \quad \text{at } X=0 \quad (41)$$

$$S_B^{(1)} = -\beta S_A^{(1)}, \quad B_B^{(1)} = \beta B_A^{(1)} \quad \text{at } X=1 \quad (42)$$

Solution of Eqs. (36)–(40) gives

$$S_A^{(1)} = \{ (1 + \gamma \delta) / (1 + \delta) \} E_1^X (1 - E_2^X) \quad (43)$$

$$S_B^{(1)} = \{ (1 + \gamma \delta) / \gamma (1 + \delta) \} E_1^X [1 - \{ 1 + \beta \gamma (1 - E_2) \} E_3^{(1-X)}] \quad (44)$$

$$A^{(1)} = B_A^{(1)} = B_B^{(1)} = 0 \quad (45)$$

in which

$$\ln E_2 = -N_A (1 + \delta) / (1 + \gamma \delta) \quad (46)$$

$$\ln E_3 = -N_A \gamma \delta (1 + \delta) / (1 + \gamma \delta) \quad (47)$$

2.3 Solution of the second-order term ($i=2$)

A procedure similar to that above leads to solution of the second-order term, of which details are given in **Appendix**. For example, the solution of $C_A^{(2)}$ is derived as

$$C_A^{(2)} = \frac{1}{2} \kappa_2 S_A^{(2)} \left(\tau^2 - \tau + \frac{1}{6} \right) + \frac{1}{12} \kappa_2 (B_A^{(2)} - S_A^{(2)}) \quad (48)$$

in which

$$\kappa_2 = \kappa_1 (1 + \gamma \delta) / (1 + \delta) \quad (49)$$

$$S_A^{(2)} = E_1^X [-N_A X E_2^X + \{\delta(\gamma - 1)/(1 + \delta)\}(1 - E_2^X)] \quad (50)$$

$$B_A^{(2)} = S_A^{(2)} + \{\delta/(1 + \delta)\} E_1^X [\gamma(1 - E_2^X) + \{1 + \beta\gamma(1 - E_2)\}(E_3^{(1-X)} - E_3) - \{(1 - \beta\gamma)/(\gamma - 1)\}(B_A^{(2)} - S_A^{(2)})(1 - E_1^X)] \quad (51)$$

and

$$B_{A1}^{(2)} - S_{A1}^{(2)} = \frac{\delta(\gamma - 1)E_1[\gamma(1 - E_2) + \{1 + \beta\gamma(1 - E_2)\}(1 - E_3)]}{(1 + \delta)\{\gamma(1 - \beta) - (1 - \beta\gamma)E_1\}} \quad (52)$$

3. Results and Discussion

In the preceding section, a perturbation solution was derived to determine the local and instantaneous behavior of four variables C_A , C_D , Q_A , Q_D of gas-phase concentrations and amounts adsorbed in both adsorption and desorption steps. The concentration of product gas stream C_{A1} is probably the most important and thus the following discussion is devoted mainly to this variable C_{A1} .

3.1 Result for product gas concentration C_{A1}

Product gas concentration C_{A1} can be evaluated by equating $X=1$, i.e.

$$C_{A1} = C_{A1}^{(0)} + \lambda C_{A1}^{(1)} + \lambda^2 C_{A1}^{(2)} \quad (53)$$

in which subscript 1 refers to $X=1$. The final result for C_{A1} up to the second-order term is summarized in **Table 1**.

Time average concentration $\overline{C_{A1}}$ during the adsorption step is given by

$$\overline{C_{A1}} = \int_0^1 C_{A1} d\tau = \overline{C_{A1}^{(0)}} + \lambda \overline{C_{A1}^{(1)}} + \lambda^2 \overline{C_{A1}^{(2)}} \quad (54)$$

The term $C_{A1}^{(0)}$ is independent of τ as given by Eq. (27) and thus

$$\overline{C_{A1}^{(0)}} = C_{A1}^{(0)} \quad (55)$$

The first-order term does not contribute to $\overline{C_{A1}}$ because of symmetric and linear change with τ . The second-order contribution $\overline{C_{A1}^{(2)}}$ leads to

$$\overline{C_{A1}^{(2)}} = \frac{1}{12} \kappa_2 (B_{A1}^{(2)} - S_{A1}^{(2)}) \quad (56)$$

which is given by Eq. (52). The difference in concentration between that at the beginning of adsorption or desorption and that at the end is called concentration swing. The concentration swing in product gas ΔC_{A1} is written as

$$\Delta C_{A1} = C_{A1}|_{\tau=1} - C_{A1}|_{\tau=0} = \Delta C_{A1}^{(0)} + \lambda \Delta C_{A1}^{(1)} + \lambda^2 \Delta C_{A1}^{(2)} \quad (57)$$

Since $C_{A1}^{(0)}$ is independent of τ and $C_{A1}^{(2)}$ is symmetric

Table 1. Result of analysis

$$\begin{aligned} &1) \text{ Instantaneous concentration in product gas stream } C_{A1} \\ &C_{A1} = C_{A1}^{(0)} + \lambda C_{A1}^{(1)} + \lambda^2 C_{A1}^{(2)} \\ &= C_{A1}^{(0)} \left[1 + \lambda M^{(1)} \left(\tau - \frac{1}{2} \right) + \lambda^2 \left\{ M^{(2)} \left(\tau^2 - \tau + \frac{1}{6} \right) + H^{(2)} \right\} \right] \end{aligned} \quad (T-1)$$

in which

$$C_{A1}^{(0)} = (1 - \eta)/(1 - \beta\eta), \quad (T-2)$$

$$\eta = (1 - E_1)/(1 - E_1/\gamma) \quad (T-3)$$

$$M^{(1)} = \kappa_1 S_{A1}^{(1)}/C_{A1}^{(0)} = \{\gamma\delta(1 - \beta)/(1 + \delta)\}(1 - E_2) \quad (T-4)$$

$$M^{(2)} = \frac{1}{2} \kappa_2 S_{A1}^{(2)}/C_{A1}^{(0)} = \frac{\gamma\delta^2(\gamma - 1)(1 - \beta)}{2(1 + \delta)^2} \left\{ 1 - E_2 - \frac{(1 + \delta)N_A E_2}{\delta(\gamma - 1)} \right\} \quad (T-5)$$

$$\begin{aligned} H^{(2)} &= \frac{\kappa_2 (B_{A1}^{(2)} - S_{A1}^{(2)})/C_{A1}^{(0)}}{12} \\ &= \frac{\gamma\delta^2(\gamma - 1)(1 - \beta)[\gamma(1 - E_2) + \{1 + \beta\gamma(1 - E_2)\}(1 - E_3)]}{12(1 + \delta)^2\{\gamma(1 - \beta) - (1 - \beta\gamma)E_1\}} \end{aligned} \quad (T-6)$$

2) Average concentration in product gas stream $\overline{C_{A1}}$

$$\overline{C_{A1}} = C_{A1}^{(0)}(1 + \lambda^2 H^{(2)}) \quad (T-7)$$

3) Amount of concentration swing in product gas stream ΔC_{A1}

$$\Delta C_{A1} = \lambda C_{A1}^{(0)} M^{(1)} \quad (T-8)$$

about $\tau=1/2$, they do not contribute to ΔC_{A1} . Concentration swing consists of only the first-order term and thus

$$\Delta C_{A1}^{(0)} = \Delta C_{A1}^{(2)} = 0 \quad (58), (59)$$

$$\Delta C_{A1}^{(1)} = \kappa_1 S_{A1}^{(1)} \quad (60)$$

which is given by Eq. (43). Average concentration $\overline{C_{A1}}$ and concentration swing ΔC_{A1} for the product gas stream are also summarized in **Table 1**.

Results for a symmetric case ($\gamma=1$) may be obtained straightforwardly by taking a limit as $\gamma \rightarrow 1$. Results for the purge gas concentration can be obtained in a similar manner.

3.2 Time dependence of product gas concentration C_{A1}

As summarized in **Table 1**, the product gas concentration C_{A1} consists of three contributions, each of which has its own particular dependence on time, i.e.

- the zeroth-order term $C_{A1}^{(0)}$ is time-independent
- the first-order term $C_{A1}^{(1)}$ is linear with time
- the second-order term $C_{A1}^{(2)}$ is parabolic.

Figure 2 shows a typical example of each contribution to product gas concentration C_{A1} for the case of $\beta=0.1$, $\gamma=5$, $\delta=0.2$ and $N_A=10$. The linear term $C_{A1}^{(1)}$ always has a positive slope given by $\kappa_1 S_{A1}^{(1)}$ and it is a point symmetric about $(1/2, 0)$. The parabolic term $C_{A1}^{(2)}$ is symmetric about $\tau=1/2$ and is concave or convex depending on a combination of parameters. Variation of product gas concentration C_{A1} with time

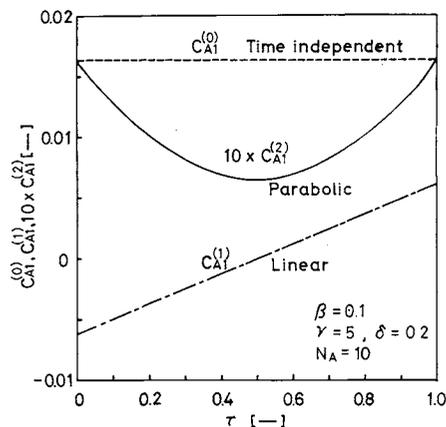


Fig. 2. Typical time dependence of perturbed terms of zeroth, first and second orders.

is obtained by summing the three contributions weighted by a factor of $\lambda^{(i)}$ according to Eq. (53). A sample calculation is given in Fig. 3 for various values of λ . Broken lines represent numerical results by the Euler method. Gas concentration does not change with time at the limit of $\lambda \rightarrow 0$ and only the time-independent term $C_{A1}^{(0)}$ is important there. For a small but finite value of λ , say $\lambda < 0.5$, the concentration changes linearly with time. Variation of C_{A1} with time can sufficiently be represented by approximation up to the first-order term, i.e.

$$C_{A1} = C_{A1}^{(0)} + \lambda C_{A1}^{(1)} \left(\tau - \frac{1}{2} \right) \quad (61)$$

which is shown by chain lines in Fig. 3. As the value of λ increases further, the value of C_{A1} begins to deviate from a straight line. Deviation from linear dependence can be corrected by Eq. (T-1), which includes the contribution of the second-order parabolic term. When the λ -value further increases beyond 2, the second-order correction becomes insufficient and higher-order approximation is necessary.

3.3 Average concentration of product gas \bar{C}_{A1}

Some typical results of average concentration \bar{C}_{A1} in the product gas stream are shown in Fig. 4 for $\beta = 0.1$, $\gamma = 5$, $\delta = 0.2$ and various values of N_A and λ . As cycle time t_c , and then the λ -value, decrease, the average concentration \bar{C}_{A1} reaches a constant limiting value at which PSA operation gives the highest performance. This trend of the asymptotic behavior agrees with the result of numerical analysis by Chihara and Suzuki.²⁾ Equation (T-2), shown by chain lines in the figure, is a solution to this limiting situation with short cycle time and agrees very well with the exact numerical solution up to $\lambda = 0.5$.

It should be noted that the quantity of η in Eq. (T-3) is equal to the mass transfer efficiency through a membrane when feed gas of concentration c_{A0} is contacted countercurrently with another gas stream

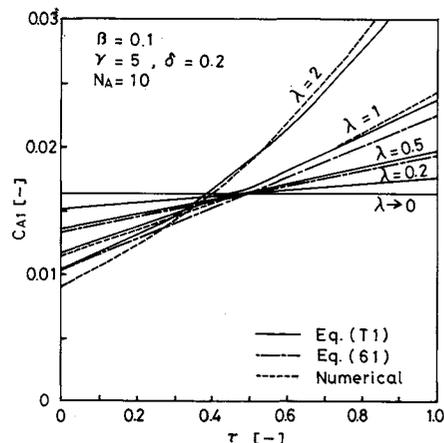


Fig. 3. Time dependence of product gas concentration.

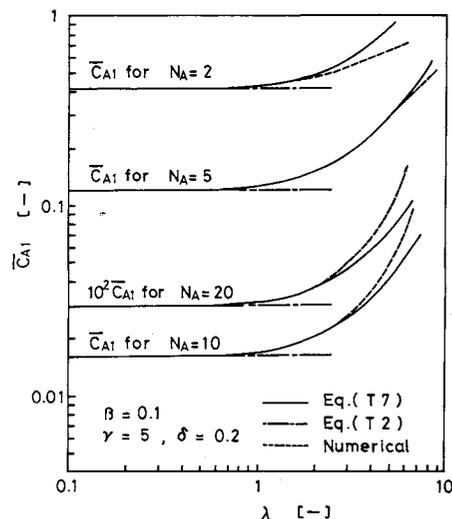


Fig. 4. Average concentration of product gas.

of concentration c_{D1} , i.e.

$$\eta = (c_{A0} - c_{A1}) / (c_{A0} - c_{D1}) \quad (62)$$

Substitution of βc_{A1} for c_{D1} and rearrangement gives Eq. (T-2) straightforwardly. Thus, the direct analogy holds between countercurrent membrane transport and PSA operation when cycle time is sufficiently short. Suzuki⁷⁾ has recently proposed a method of computer simulation for this situation.

Equation (T-2) is reduced to

$$C_{A1}^{(0)} = \frac{\gamma - 1}{\gamma(1 - \beta)} \exp \left\{ -\frac{\delta(\gamma - 1)}{1 + \gamma\delta} N_A \right\} \quad (63)$$

for large positive values of $(\gamma - 1)N_A$. In this region, the product concentration \bar{C}_{A1} is greatly influenced by number of transfer units N_A , as shown in Fig. 4, because it decreases exponentially with increasing N_A according to Eq. (63).

As the λ -value increases beyond 0.5, the exact value deviates from the limiting solution Eq. (T-2) but this deviation is evaluated by the second-order approximation Eq. (T-7), which may be valid for $\lambda < 2$.

3.4 Concentration swing ΔC_{A1}

The concentration swing is another important indicator to characterize the performance of PSA. Some examples of results for the concentration swing in the product gas stream are shown in Fig. 5, again for $\beta=0.1$, $\gamma=5$, $\delta=0.2$. When λ is small in a short cycle time operation, the concentration swing is proportional to λ as shown in the figure. Equation (T-8) will represent this dependence quantitatively. The effect of N_A on ΔC_{A1} is very large and similar to that on C_{A1} . For large values of N_A , the relative swing $M^{(1)}$, Eq. (T-4), is reduced to

$$M^{(1)} = \gamma\delta(1-\beta)/(1+\delta) \quad (64)$$

which is independent of N_A . Thus, concentration swing is directly proportional to $C_{A1}^{(0)}$.

3.5 Criterion of applicability

As shown by sample calculations in the preceding sections the present analysis is found to be an accurate approximation if the value of λ is less than about 2. Further, the second-order term may be safely neglected for $\lambda < 0.5$. This criterion for applicability of the present analysis was confirmed with various sets of parameters other than shown in Figs. 3-5. The parameter λ is rewritten as

$$\lambda = \frac{K_A a m L / u_A}{m \rho_s L / u_A t_c} = \frac{N_A}{n_A} \quad (65)$$

in which n_A is a ratio of adsorption capacity to feed volume. The above criterion ($\lambda < 2$) means that n_A must be greater than $N_A/2$. For example, $n_A > 10$ at $N_A = 20$.

Conclusion

A set of partial differential equations describing the gas concentration and amount adsorbed of PSA operated at periodic steady state was expanded into power series functions of small value of λ and a solution was derived up to the second-order term. The final result of analysis for the product gas concentration is shown in Table 1.

The zeroth order term is independent of time. The first-order term is linear with time and contributes to the concentration swing though it does not contribute to the time average product gas concentration. The second-order term is parabolic with time and contributes to a second-order correction of the average concentration but not to the concentration swing.

It is found that the present analysis is an accurate approximation when half-cycle time is short enough to satisfy the criterion of $\lambda < 2$. The second-order correction can be safely neglected if $\lambda < 0.5$.

Appendix. Derivation of the second-order term

In a similar manner to the first-order solution in 2.2, time dependence of $C^{(2)}$ and $Q^{(2)}$ takes the form of

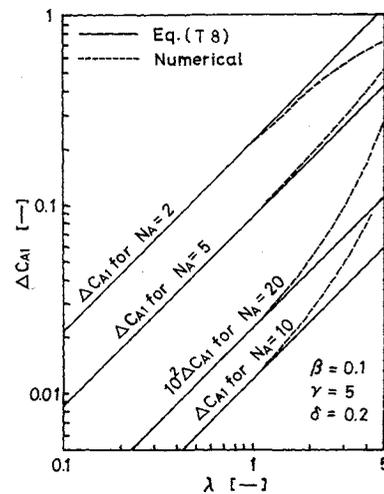


Fig. 5. Concentration swing of product gas.

$$Q_A^{(2)} = \frac{1}{2} \kappa_2 G_A^{(2)} \left(\tau^2 - \tau + \frac{1}{6} \right) + \frac{1}{12} \kappa_2 (A^{(2)} - G_A^{(2)}) \quad (A-1)$$

$$Q_B^{(2)} = \frac{1}{2} \kappa_2 G_B^{(2)} \left(\tau^2 - 3\tau - \frac{13}{6} \right) + \frac{1}{12} \kappa_2 (A^{(2)} - G_B^{(2)}) \quad (A-2)$$

$$C_A^{(2)} = \frac{1}{2} \kappa_2 S_A^{(2)} \left(\tau^2 - \tau + \frac{1}{6} \right) + \frac{1}{12} \kappa_2 (B_A^{(2)} - S_A^{(2)}) \quad (A-3)$$

$$C_B^{(2)} = \frac{1}{2} \kappa_2 S_B^{(2)} \left(\tau^2 - 3\tau - \frac{13}{6} \right) + \frac{1}{12} \kappa_2 (B_B^{(2)} - S_B^{(2)}) \quad (A-4)$$

In Eqs. (A-1)–(A-4), functions $A^{(2)}$, $B_A^{(2)}$, $B_B^{(2)}$, $S_A^{(2)}$ and $S_B^{(2)}$ depend on X only and satisfy the following equations:

$$G_A^{(2)} = E_1^X \{ \delta(\gamma-1)/(1+\gamma\delta) - E_2^X \} \quad (A-5)$$

$$G_B^{(2)} = E_1^X \{ \delta(\gamma-1)/(1+\gamma\delta) \} + \delta \{ 1 + \beta\gamma(1-E_2) \} E_3^{(1-X)} \quad (A-6)$$

In Eqs. (A-1)–(A-4), functions $A^{(2)}$, $B_A^{(2)}$, $B_B^{(2)}$, $S_A^{(2)}$ and $S_B^{(2)}$ depend on X only and satisfy the following equations:

$$dS_A^{(2)}/dX = -N_A(S_A^{(2)} - G_A^{(2)}) \quad (A-7)$$

$$dS_B^{(2)}/dX = N_B(S_B^{(2)} - G_B^{(2)}) \quad (A-8)$$

$$dB_A^{(2)}/dX = -N_A(B_A^{(2)} - A^{(2)}) \quad (A-9)$$

$$dB_B^{(2)}/dX = N_B(B_B^{(2)} - A^{(2)}) \quad (A-10)$$

$$(S_A^{(2)} - G_A^{(2)}) + \gamma\delta(S_B^{(2)} - G_B^{(2)}) = (B_A^{(2)} + \gamma\delta B_B^{(2)}) - (1+\gamma\delta)A^{(2)} \quad (A-11)$$

When they are solved using boundary conditions same as Eqs. (41) and (42) with superscript (1) replaced by (2) , one gets Eqs. (50) and (51) for $S_A^{(2)}$ and $B_A^{(2)}$ and the following functions for $S_B^{(2)}$ and $B_B^{(2)}$:

$$S_B^{(2)} = E_1^X \{ \delta(\gamma-1)/\gamma(1+\delta) + \delta^2 N_A \{ 1 + \beta\gamma(1-E_2) \} (1-X) E_3^{(1-X)} + \{ \delta/(1+\delta) \} \{ (\gamma-1)(\beta-1/\gamma) - \beta(N_A(1+\delta)/\delta + \gamma-1) E_2 \} E_3^{(1-X)} \} \quad (A-12)$$

$$B_B^{(2)} = (1/\gamma) [B_A^{(2)} - (S_A^{(2)} - \gamma S_B^{(2)}) - (1-\beta\gamma)(B_A^{(2)} - S_A^{(2)})] \quad (A-13)$$

in which $B_A^{(2)} - S_A^{(2)}$ is given by Eq. (52). Function $A^{(2)}$ is derived by Eq. (A-11) by substituting $S_A^{(2)}$, $S_B^{(2)}$, $B_A^{(2)}$ and $B_B^{(2)}$ thus obtained.

Nomenclature

$A^{(1)}, A^{(2)}$	= functions of X to be determined	[—]
a	= specific mass transfer area	[m ² /m ³]
$B^{(1)}, B^{(2)}$	= functions of X to be determined	[—]
C	= dimensionless concentration (= c/c_{A0})	[—]
\overline{C}_{A1}	= average concentration of product gas	[—]

ΔC_{A1}	= concentration swing of product gas	[—]	η	= defined by Eq. (28) or Eq. (T-5)	[—]
c	= concentration of adsorbate gas	[mol/m ³]	λ	= defined by Eq. (15)	[—]
E_1, E_2, E_3	= functions defined by Eqs. (29), (46) and (47), respectively	[—]	ρ_s	= bulk density of bed	[kg/m ³]
$G^{(1)}, G^{(2)}$	= functions of X to be determined	[—]	τ	= dimensionless time defined by Eq. (12)	[—]
$H^{(2)}$	= function defined by Eq. (T-6)	[—]	κ_1, κ_2	= defined by Eqs. (32) and (49)	[—]
i	= integer	[—]	<Subscripts>		
K	= overall mass transfer coefficient based on solid phase driving force (= $1/(1/k_s + m/k_f)$)	[kg/m ² s]	A, D	= adsorption step and desorption step	
k_f, k_s	= gas-phase and solid-phase mass transfer coefficient	[m/s], [kg/m ² s]	0, 1	= $x=0$ (bottom) and $X=L$ (top)	
L	= column length	[m]	<Superscripts>		
$M^{(1)}, M^{(2)}$	= functions defined by Eqs. (T-4) and (T-5)	[—]	(0),(1),(2),(i)	= zeroth, first, second and i -th order term in expansion	
m	= adsorption coefficient, $(q/c)_{\text{equil.}}$	[m ³ /kg]	—	= time average value	
N	= number of mass transfer units defined by Eq. (14)	[—]	Literature Cited		
n	= capacity ratio defined by Eq. (65), (= $m\rho_s L/u_A t_c$)	[—]	1)	Carter, J. W. and M. L. Wyszynski: <i>Chem. Eng. Sci.</i> , 38 , 1093 (1983).	
p	= pressure in column	[Pa]	2)	Chihara, K. and M. Suzuki: <i>J. Chem. Eng. Japan</i> , 16 , 53 (1983).	
Q	= dimensionless amount adsorbed (= q/mc_{A0})	[—]	3)	Chihara, K. and M. Suzuki: <i>J. Chem. Eng. Japan</i> , 16 , 293 (1983).	
q	= amount adsorbed	[mol/kg]	4)	Kawazoe, K. and T. Kawai: <i>Kagaku Kōgaku</i> , 37 , 288 (1973).	
$S^{(1)}, S^{(2)}$	= functions of X to be determined	[—]	5)	Mitchell, J. E. and L. H. Shendalman: <i>AIChE Symp. Ser.</i> , 69 , No. 134, 25 (1973).	
t	= time	[s]	6)	Raghavan, N. S., M. M. Hassan and D. M. Ruthven: <i>AIChE J.</i> , 31 , 385 (1985).	
t_c	= half cycle time	[s]	7)	Suzuki, M.: <i>AIChE Symp. Ser.</i> , 81 , No. 242, 67 (1985).	
u	= superficial gas velocity	[m/s]	(A part of this work was presented at the 18th Autumn Meeting of The Society of Chemical Engineers, Japan, at Fukuoka, 1984.)		
x	= distance from feed inlet	[m]			
X	= dimensionless distance (= x/L)	[—]			
β	= p_D/p_A	[—]			
γ	= u_D/u_A	[—]			
δ	= N_D/N_A	[—]			
ε	= void fraction	[—]			