CONSTANT-PATTERN SOLUTIONS OF FIXED-BED HYDRIDING PROCESSES WITH A MATERIAL HAVING A PLATEAU PRESSURE ON EQUILIBRIUM ISOTHERM

SATOSHI FUKADA AND NOBUO MITSUISHI
Department of Nuclear Engineering, Kyushu University, Fukuoka 812

Key Words: Absorption, Breakthrough Curve, Constant Pattern, Fixed Bed, Hydriding, Hydrogen, Mass Transfer, Metal Hydride, Metallic Particle, Plateau Pressure

A theoretical study of asymptotic solutions (constant-pattern solutions) of fixed-bed hydriding processes is presented for systems with finite longitudinal dispersion in a bed and finite resistances to mass transfer. A closed form of the solutions is obtained under conditions where a metal hydride has a plateau pressure on its equilibrium isotherm. If the equilibrium isotherm does not intersect a straight line connecting two points of an influent condition and an initial one of the bed on an x–y_m diagram, a single asymptotic mass transfer zone propagates through the bed. On the other hand, if the isotherm does intersect the line, a twin asymptotic mass transfer zone propagates. Then a plateau zone is formed between the two zones. Application to a titanium hydride bed demonstrates the usefulness of the analytical results on the basis of the asymptotic solutions.

Introduction

The existence and uniqueness of asymptotic solutions (constant-pattern solutions) has been mathematically proved for fixed-bed separation processes with Langmuir- or Freundlich-type adsorption isotherm[1,7]. The existence condition for asymptotic solutions of adsorption processes is expressed as $d^2y_i/dx_i^2<0$. A fixed bed of metallic particles, on the other hand, has been used to selectively remove hydrogen from a hydrogen-inert gas mixture in a tritium-handling glovebox. Most metal hydrides have one or two

* Received January 14, 1991. Correspondence concerning this article should be addressed to S. Fukada.

plateau pressures on the isotherm[2,3]. Thus there exist some points with an infinite value in the derivative of the equilibrium isotherm, *i.e.*, the x_i–y_i diagram. This means that the first derivative of the isotherm is not a monotone decreasing function. Therefore, some modifications of the existence condition should be made for asymptotic solutions of hydriding processes by means of a fixed bed of metallic particles. In this paper, the existence, uniqueness and important characteristics of a single or twin asymptotic mass transfer zones are analytically studied for a typical system having a plateau pressure on the equilibrium isotherm. A closed form of analytical equations is obtained for the system including finite longitudinal dispersion and finite resistances to mass transfer. Further, the application to a titanium hydride bed may demonstrate the usefulness of the analytical results on the basis of the asymptotic solutions.

1. Governing Equation

1.1 Equilibrium isotherm

The equilibrium isotherm for a typical metal-hydrogen system having only one plateau pressure such as β-phase hydrides can be classified into three regions[3]:

a solid-solution phase:

$$x_i = x_{plat}\left(\frac{y_i}{y_l}\right)^{1/n} \quad \text{for } y_i < y_l \tag{1}$$

a two-phase region:

$$x_i = x_{plat} \quad \text{for } y_l \leqq y_i \leqq y_u \tag{2}$$

a metal hydride phase:

$$x_i = x_{plat}^{1-y_i/1-y_u} \quad \text{for } y_i > y_u \tag{3}$$

The value of n in Eq. (1) is 0.5 for an ideal solid-solution phase[6]. Eq. (3) is valid for some metal-hydrogen systems, *e.g.*, Y–H_2[4] and Ti–H_2[5]. Here, x_{plat} is a dimensionless plateau hydrogen concentration in the fluid phase. y_l and y_u are values at lower and upper limits of a two-phase coexistence region on the basis of the hydrogen concentration in solid particles. Any of these values is given as a function of temperature on the phase digram[4,6].

It is noted in Eqs. (1) to (3) that x_i is a continuous single-valued function of y_i. Thus in this paper the equilibrium isotherm is generally expressed by $x_i = f(y_i)$. The function $f(y_i)$ has the conditions of $f' \geqq 0$ and $f'' \geqq 0$ in the domain of $y_i \geqq 0$. It also has discontinuous first and second derivatives at $y_i = y_l$ and $y_i = y_u$. In particular, the equality sign in the equations of $f' \geqq 0$ and $f'' \geqq 0$ is valid only at $y_i = 0$ and between $y_l \leqq y_i \leqq y_u$. Their derivatives are always positive in other regions.

1.2 Material balance equation

Dimensionless equations of the material balance and the hydriding rate are written as follows[3]:

$$\frac{1}{Pe_h}\frac{\partial^2 x}{\partial Z^2} = \frac{\partial x}{\partial Z} + \frac{1}{m}\frac{\partial x}{\partial \tau} + \frac{\partial y_m}{\partial \tau} \tag{4}$$

$$\frac{\partial y_m}{\partial \tau} = \xi_{comp}(x - x_i) = \xi_s g(y_i, y_m) \tag{5}$$

The boundary conditions are given as follows.

$$Z = -\infty \quad x = x_L = f(y_L), \quad \frac{\partial x}{\partial Z} = 0 \tag{6}$$

$$Z = \infty \quad x = x_R = f(y_R), \quad \frac{\partial x}{\partial Z} = 0 \tag{7}$$

Here, ξ_{comp} is a dimensionless parameter which comprises the resistance of the fluid-film diffusion and that of the hydriding reaction on surfaces defined in the previous works.[2,4].

2. Asymptotic Breakthrough Curve

2.1 Single asymptotic mass transfer zone

The necessary and sufficient condition for the existence of a single asymptotic mass transfer zone is equivalent to the existence of the following moving coordinate axis η[7]:

$$\eta = Z - \lambda\tau \tag{8}$$

Reducing Eqs. (4) and (5) to ordinary differential equations by Eq. (8) and integrating them with the boundary conditions of Eqs. (6) and (7), one can obtain the following pair of equations:

$$\frac{dx}{d\eta} = \lambda Pe_h F(x, y_m; x_R, y_R, x_L, y_L) = G(x, y_m) \tag{9}$$

$$\frac{dy_m}{d\eta} = -\frac{\xi_{comp}}{\lambda}(x - x_i) = -\frac{\xi_s}{\lambda}g(y_i, y_m) = H(x, y_m) \tag{10}$$

in which the function F is defined as follows:

$$F(x, y_m; x_R, y_R, x_L, y_L) = (y_L - y_R)\frac{x - x_R}{x_L - x_R} - (y_m - y_R) \tag{11}$$

The propagation velocity of the single mass transfer zone, λ, is obtained as follows:

$$\frac{1}{\lambda} = \frac{1}{m} + \frac{y_L - y_R}{x_L - x_R} \tag{12}$$

It should be specified that functions of $G(x, y_m)$ and $H(x, y_m)$ defined in Eqs. (9) and (10) are continuous in the domain of all positive x and y_m values, while the first derivatives have some discontinuity. Then the existence and uniqueness of the solutions to Eqs. (9)

and (10) is assured for any set of given initial values of x and y_m at a specified η value, since the functions G and H are integrable in the domain of $x \geqq 0$ and $y \geqq 0$. The intersections of the lines $G=0$ and $H=0$ are just two points, which are now expressed as the point $R(x_R, y_R)$ and the point $L(x_L, y_L)$. The points R and L are both singular points. The curve $H=0$ gives the equilibrium isotherm, *i.e.*, $x_i = f(y_i)$. The line $G=0$ gives a straight line connecting the two singular points, which is also depicted as an operating line for an infinite Pe_h value.

The nature of the direction field in the neighborhood of the singular points is now examined. We further suppose the condition of $y_L > y_R$, where y_L is in the β-hydride phase and y_R in the solid-solution phase. This may be a general hydriding process by means of a metallic particle bed. Then the characteristic equation of the system expressed by Eqs. (9) and (10) is given by

$$\begin{vmatrix} \dfrac{\partial G}{\partial x} - \beta, & \dfrac{\partial G}{\partial y_m} \\ \dfrac{\partial H}{\partial x}, & \dfrac{\partial H}{\partial y_m} - \beta \end{vmatrix} = 0 \tag{13}$$

Unfortunately, the roots of the characteristic equation cannot be analytically obtained, since the function $g(y_i, y_m)$ in Eq. (10) has a complicated formula[3]. Therefore, an approximation of linear driving force is used in place of $g(y_i, y_m)$:

$$\frac{dy_m}{d\eta} = -\frac{\xi_{comp}}{\lambda}(x - x_i) = -\frac{\xi_s}{\lambda}(y_i - y_m) = H(x, y_m) \tag{14}$$

It is believed that the use of the linear driving force approximation does not lose the generality of the proof of the existence and uniqueness of the solutions to the metal-hydrogen system with a plateau pressure.

Then the two roots $\beta_\pm$ are obtained as follows:

$$\begin{aligned} \beta_\pm = & \frac{\xi_{comp}\xi_s f'}{2\lambda(\xi_{comp} f' + \xi_s)} + \frac{\lambda Pe_h}{2}\left(\frac{1}{\lambda} - \frac{1}{m}\right) \\ & \pm \left[\left\{ \frac{\xi_{comp}\xi_s f'}{2\lambda(\xi_{comp} f' + \xi_s)} + \frac{\lambda Pe_h}{2}\left(\frac{1}{\lambda} - \frac{1}{m}\right) \right\}^2 \right. \\ & \left. - \frac{Pe_h \xi_{comp}\xi_s}{\xi_{comp} f' + \xi_s} \left\{ f'\left(\frac{1}{\lambda} - \frac{1}{m}\right) - 1 \right\} \right]^{1/2} \end{aligned} \tag{15}$$

It is proved that both β_+ and β_- are real because the discriminant of Eq. (13) is always positive. It is also noticed that $f' > (x_L - x_R)/(y_L - y_R)$ and thus $\beta_+ > \beta_- > 0$ at point L, whereas $f' < (x_L - x_R)/(y_L - y_R)$ and thus $\beta_+ > 0 > \beta_-$ at point R. Consequently, L is found to be an unstable node and R a saddle point[8].

The solid line in **Fig. 1** shows an example of an

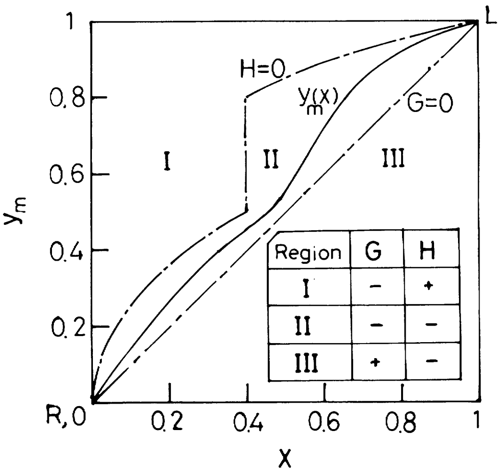

Fig. 1. Integral curve and lines of $G=0$ and $H=0$ with single mass transfer zone
($Pe_h/\xi_{comp} = 1$, $\xi_{comp} = \xi_s$, $x_{plat} = 0.4$, $y_l = 0.5$, $y_u = 0.8$)

integral curve $y_m(x)$, where $x_R = 0$ as an initial condition and $x_L = 1$ as an influent condition are assumed. The curve is also called an operating line in mass transfer operation. The curves of $H=0$ and $G=0$ and the signs of functions $G(x, y_m)$ and $H(x, y_m)$ in the domain of $0 \leqq x \leqq 1$ and $0 \leqq y_m \leqq 1$ are also shown in Fig. 1. Since the integral curve $y_m(x)$ is a monotone increasing function, the sign of the ratio H/G should always be positive, judging from Eqs. (9) and (10). In the region II, intercepted by the relations of $G=0$ and $H=0$ in the figure, their signs are both negative. On the other hand they differ in sign in regions I and III. Thus the integral curve always remains in region II. The integral curve converges to point R (0, 0) as η approaches ∞ and to point L (1, 1) as η approaches $-\infty$. The lines of $y_m(x)$ asymptotically converge to line $G=0$ as the Pe_h value approaches infinity. They converge to the curve $H=0$ as the Pe_h value approaches zero or the values of both ξ_{comp} and ξ_s approach infinity. In conclusion, a single asymptotic mass transfer zone is formed in a fixed bed of sufficient height when the equilibrium isotherm $f(y_i)$ satisfies the conditions $f' \geqq 0$ and $f'' \geqq 0$ and does not intersect the straight line connecting the two points (x_R, y_R) and (x_L, y_L). Then the breakthrough curve for the hydriding process is similar to that for adsorption.

2.2 Twin asymptotic mass transfer zone

When the isotherm intersects the straight line connecting the two points R and L, the mass transfer zone may be split into two stages according to position above and below the point (x_{plat}, y_l) on the equilibrium isotherm. The first mass transfer zone in the range of $x_R \leqq x < x_{plat}$ is located in front of the second one in the range of $x_{plat} < x \leqq x_L$. Then, two kinds of moving coordinate axes are defined as η_1 and η_2:

$$\eta_k = Z - \lambda_k \tau \qquad k=1,2 \tag{16}$$

The boundary conditions for each mass transfer zone are given by

$$\eta_1 = -\infty \quad x = x_{plat} = f(y_l), \quad \frac{\partial x}{\partial \eta_1} = 0 \tag{17}$$

$$\eta_1 = \infty \quad x = x_R = f(y_R), \quad \frac{\partial x}{\partial \eta_1} = 0 \tag{18}$$

$$\eta_2 = -\infty \quad x = x_L = f(y_L), \quad \frac{\partial x}{\partial \eta_2} = 0 \tag{19}$$

$$\eta_2 = \infty \quad x = x_{plat} = f(y_l), \quad \frac{\partial x}{\partial \eta_2} = 0 \tag{20}$$

The propagation velocities of each mass transfer zone are obtained by a similar procedure to that described above:

$$\frac{1}{\lambda_1} = \frac{1}{m} + \frac{y_l - y_R}{x_{plat} - x_R} \tag{21}$$

$$\frac{1}{\lambda_2} = \frac{1}{m} + \frac{y_L - y_l}{x_L - x_{plat}} \tag{22}$$

Eqs. (4) and (5) are rewritten for each mass transfer zone:

$$\frac{dx}{d\eta_k} = G_k(x, y_m), \qquad k=1,2 \tag{23}$$

$$G_1(x, y_m) = \lambda_1 Pe_h F(x, y_m; x_R, y_R, x_{plat}, y_l) \tag{24}$$

$$G_2(x, y_m) = \lambda_2 Pe_h F(x, y_m; x_{plat}, y_l, x_L, y_L) \tag{25}$$

$$\frac{dy_m}{d\eta_k} = -\frac{\xi_{comp}}{\lambda_k}(x - x_i) = -\frac{\xi_s}{\lambda_k}(y_i - y_m) = H_k(x, y_m), \qquad k=1,2 \tag{26}$$

The intersections of the relations $G_1=0$ and $H_1=0$ are just two: (x_R, y_R) and (x_{plat}, y_l). The former is found to be a saddle point by a similar procedure to that described above. The later is an unstable node. The isotherm between $y_R \leqq y_i \leqq y_l$ is convex when it is observed from the x-axis (because it has the derivatives $f'>0$ and $f''>0$). Therefore, the existence and uniqueness of the asymptotic solutions is assured on the basis of the existence condition for the adsorption process[1,7] depicted as $d^2y_i/dx_i^2<0$. Thus integral curves are always present in the region intersected by both lines $G_1=0$ and $H_1=0$. Similarly, the intersections of lines $G_2=0$ and $H_2=0$ are also two: (x_{plat}, y_l) of a saddle point and (x_L, y_L) of an unstable node. As the isotherm between $y_l \leqq y_i \leqq y_L$ is also convex, the existence and uniqueness of the asymptotic solutions is assured. Thus integral curves are always present in the region intersected by both lines $G_2=0$ and $H_2=0$.

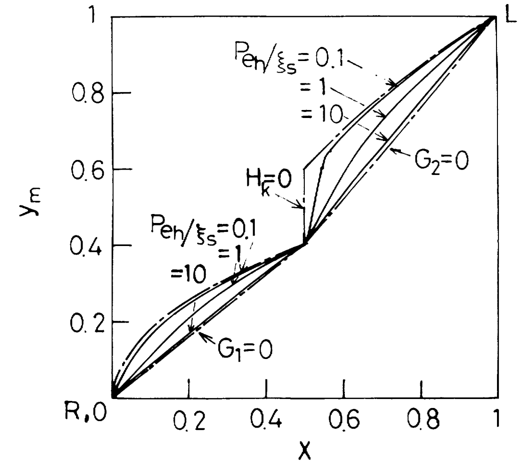

Fig. 2. Integral curves with twin mass transfer zones ($\xi_{comp}=\xi_s$, $x_{plat}=0.5$, $y_l=0.4$, $y_u=0.6$)

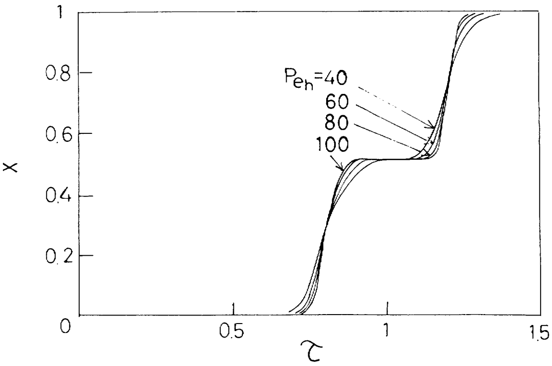

Fig. 3. Asymptotic breakthrough curves with twin mass transfer zones ($\xi_{comp}=\xi_s=100$, $x_{plat}=0.5$, $y_l=0.4$, $y_u=0.6$, $m=1000$)

Figure 2 is an illustration of operating lines for some values of Pe_h and ξ_s under $\xi_{comp}=\xi_s$. Each operating line for the first and second mass transfer zones varies with the values of a parameter Pe_h/ξ_s. It asymptotically converges to the equilibrium isotherm as values of both Pe_h/ξ_s and Pe_h/ξ_{comp} approach zero. If both of them approach infinity, the operating line of the first mass transfer zone converges to the line $G_1=0$ and that of the second mass transfer zone to the line $G_2=0$.

2.3 Example of breakthrough curve with plateau zone

Figure 3 shows numerical examples of asymptotic breakthrough curves with twin mass transfer zones. In the asymptotic curves, each propagation velocity of the first and the second mass transfer zones is constant regardless of the values of Pe_h, ξ_{comp} and ξ_s. It depends on the plateau concentration on the equilibrium isotherm, the influent conditions of a fixed bed and initial ones. An interval of the plateau zone on the breakthrough curves may increase in proportion to the bed height due to the difference between the two propagation velocities.

Figure 4 shows some examples of experimental

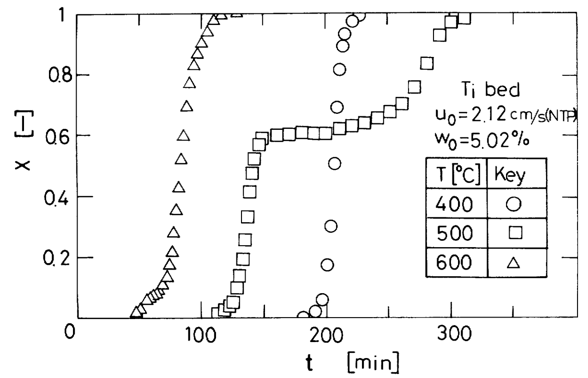

Fig. 4. Experimental breakthrough curves of titanium particle bed

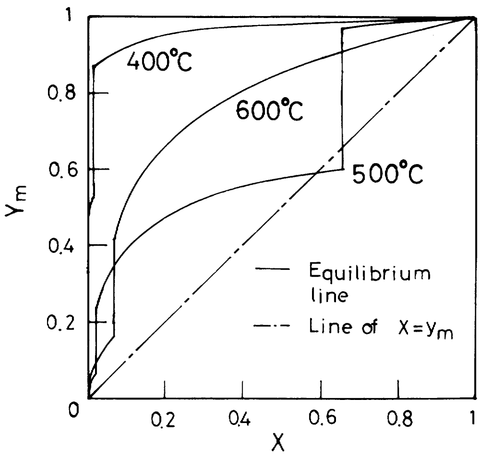

Fig. 5. x–y_m diagram of titanium-hydrogen system

breakthrough curves of a titanium particle bed. The curves were obtained by using the apparatus described in the previous paper[4]. When the column temperature is 400°C, there is no plateau zone in the breakthrough curve, as shown in the figure. On the other hand, one plateau zone appears in the curve when the column temperature is 500°C at the same influent condition. The hydrogen concentration in the plateau zone is in good agreement with that calculated from the plateau pressure corresponding to formation of the δ-phase from the β-phase of titanium[6]. Further, there is a reflection point in the breakthrough curve at the condition of 600°C which fits the pressure corresponding to formation of the β-phase from the α-phase of titanium[6].

The equilibrium lines for each experimental condition are shown in **Fig. 5**. It is confirmed that the breakthrough curve at 500°C may have one plateau zone even in the asymptotic condition because the equilibrium line intersects the line of $x=y_m$ in the figure. On the other hand, when $T=600$°C, the plateau zone may disappear at the asymptotic breakthrough curve even if the zone or the inflection point appears in the developing effluent curve from a bed with an insufficient height. It is apparent that the x–y_m diagram is a useful tool for determining the existence and the characteristics of the asymptotic plateau zone.

Conclusion

The asymptotic solutions of fixed-bed hydriding processes are obtained under the condition where the equilibrium isotherm of a metal-hydrogen system has a plateau pressure. The existence condition of the solutions is determined on the basis of an x–y_m diagram. If the equilibrium isotherm does not intersect the line which connects the points of the initial and the influent conditions of the bed on the x–y_m diagram, a single mass transfer zone propagates through the bed. If the equilibrium isotherm intersects the line, twin asymptotic mass transfer zones are formed regardless of the values of Pe_h, ξ_{comp} and ξ_s. Then a plateau zone is formed in the bed due to the difference in propagation velocities. The existence of the plateau zone is confirmed by the experiment using a titanium particle bed. It is evident that the asymptotic solutions obtained here are a useful tool for obtaining the characteristics of the effluent curves of a fixed bed of metal particles.

Nomenclature

a_v	= external particle area per unit volume of fixed bed	[l/m]
c	= hydrogen concentration in fluid phase	[mol/m^3]
D_L	= longitudinal dispersion coefficient	[m^2/s]
$F(x, y_m; x_R, y_R, x_L, y_L)$	= function defined by Eq. (11)	[—]
$f(y_i)$	= equilibrium isotherm	[—]
f'	= dx_i/dy_i, ($f''=d^2x_i/dy_i^2$)	[—]
$G(x, y_m)$	= function defined by Eq. (9), or Eqs. (24) and (25)	[—]
$g(y_i, y_m)$	= solution of the moving-boundary problem defined in the reference[3]	[—]
$H(x, y_m)$	= function defined by Eq. (10) or Eq. (26)	[—]
h	= height of fixed bed	[m]
k_{comp}	= composite mass transfer coefficient	[m/s]
k_s	= internal mass transfer coefficient	[m/s]
m	= $\gamma q_0/\varepsilon c_0$	[—]
n	= constant	[—]
Pe_h	= $uh/\varepsilon D_L$	[—]
q	= hydrogen concentration in solid phase	[—, H/Metal]
t	= time	[s]
u	= superficial fluid velocity	[m/s]
w_0	= inlet hydrogen mole fraction	[—]
x	= c/c_0	[—]
y	= q/q_0	[—]
z	= axial distance in flow direction	[m]
Z	= z/h	[—]
β	= root of characteristic equation	[—]
γ	= bed molar density	[mol/m^3]
ε	= void fraction of fixed bed	[—]
η	= dimensionless moving coordinate	[—]
λ	= dimensionless propagation velocity of mass transfer zone	[—]
ξ_{comp}	= $hk_{comp}a_v/u$	[—]
ξ_s	= $h\gamma q_0 k_s a_v/uc_0$	[—]
τ	= $uc_0t/h\gamma q_0$	[—]

⟨Subscripts⟩

comp	=	composite
i	=	interface value
L	=	condition at $z=-\infty$
l	=	lower limit of two-phase region
m	=	mean
plat	=	plateau value
R	=	condition at $z=+\infty$
s	=	solid phase
u	=	upper limit of two-phase region
0	=	influent condition
1	=	first mass transfer zone
2	=	second mass transfer zone

Literature Cited

1) Cooney, D. O. and E. N. Lightfoot: *I&EC Fundam.*, **4**, 233 (1965).
2) Fukada, S., S. Kitajima and N. Mitsuishi: *J. Nucl. Sci. Technol.*, **25**, 895 (1988).
3) Fukada, S. and N. Mitsuishi: *J. Chem. Eng. Japan*, **24**, 106 (1991).
4) Fukada, S.: T. Nakahara and N. Mitsuishi: *J. Chem. Eng. Japan*, **24**, 113 (1991).
5) Fukada, S.; *Dr. Thesis*, Kyushu University, Fukuoka, Japan (1989).
6) Mueller, W. M., J. P. Blackledge and G. G. Linbowitz: "Metal Hydrides", Academic Press, New York, (1968).
7) Rhee, H. K. and N. R. Amundson: *Chem. Eng. Sci.*, **27**, 199 (1972).
8) Coddington, E. A. and N. Levinson: "Theory of Ordinary Differential Equations", McGraw-Hill, New York, (1955).