

# EFFECT OF PLATEAU PRESSURES ON ABSORPTION BREAKTHROUGH CURVES OF HYDROGEN WITH YTTRIUM PARTICLE BEDS —EXPERIMENTAL WORK—

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## Introduction

In the previous paper<sup>1)</sup>, a numerical investigation of the effect of plateau pressures on absorption breakthrough curves of hydrogen with metallic particle beds was reported and the emergence of a plateau zone on breakthrough curves was discussed. In the present work an experimental work was carried out on mass transfer in metallic particle beds when the inlet concentration of hydrogen is higher than the plateau concentration. The material used in this experiment is yttrium, the hydride of which has a plateau pressure of 0.3 mmHg at around 800°C. The experimental results for yttrium were compared with the analytical ones in the previous paper<sup>1)</sup>. The equilibrium isotherm of the yttrium-hydrogen system and parameters such as the mass transfer coefficient are given in **Appendix 1** and **Appendix 2** respectively.

## 1. Experimental

Yttrium used in this research work was from Kojundo Chemical Co. in Japan. Its stated purity was more than 99.9% with the following impurities: Fe 100 ppm, Ca 90 ppm, Si 80 ppm, Na 50 ppm, Ni 20 ppm, Cr 10 ppm, and Sn 7 ppm. Yttrium was crushed in a glove box under an atmosphere of high-purity argon. Yttrium particles of 80–120 mesh, weighing 1.47 to 4.00 g, were packed in each quartz glass column in the argon glove box in order to avoid contact with air.

The purities of the gases used in the experimental work were as follows: H<sub>2</sub>, 99.99999%; Ar, 99.9995%.

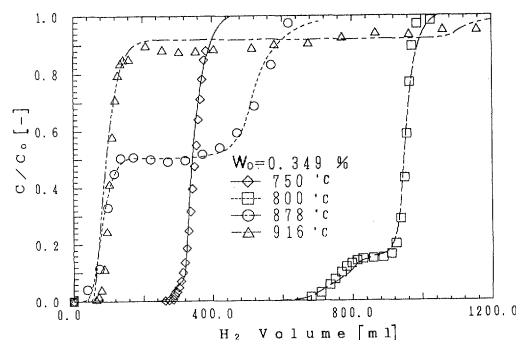
The experimental apparatus and the procedure have already been described<sup>3)</sup>. The inside diameter of the column was 10 mm and the packed height was 0.80 to 2.50 cm. The hydrogen content in Ar gas at the outlet of the bed was analyzed by gas chromatography. The experimental conditions were  $u_m=0.99$  to 41.6 cm/s (NTP),  $T=750$  to 916°C and  $w_0=0.031$  to

5.02%.

## 2. Experimental Results and Discussion

**Figure 1** shows typical results of experimental breakthrough curves of yttrium. The abscissa ( $=c/c_0$ ) represents the ratio of the outlet concentration to the inlet concentration and the ordinate the hydrogen amount fed from the inlet. The inlet molar fraction of hydrogen,  $w_0$ , was 0.349% in the runs, and the bed height was 1.20 cm for the runs of  $T=750$ , 878 and 916°C and 2.50 cm for  $T=800$ °C.

As the bed temperature is lowered, the width of the plateau zone in the figure becomes shorter. We define the time interval of the plateau zone as the time interval in which the dimensionless outlet concentration is constant within 1% except at  $c/c_0=0$  or 1. As the value of  $c_{plat}$  on the equilibrium isotherm decreases, i.e., the bed temperature becomes lowered, the time interval of the plateau zone decreases. Finally, at  $T=750$ °C, there exists no plateau zone on the breakthrough curve, because the operating line for the runs at a temperature higher than  $T=750$ °C intersects the straight line connecting (0,0) and (1,1) on the  $c/c_0-q_m/q_0$  diagram as described in the previous paper<sup>1)</sup>, while that at 750°C does not intersect the line. Here,  $q_m/q_0$  is the ratio of the mean solid-phase concentration to the solid-phase concentration in



**Fig. 1.** Experimental breakthrough data and numerical curves

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equilibrium with  $c_0$ . If we aim at recovering hydrogen to a very low concentration by using materials with plateau pressures on the equilibrium isotherm, we should not operate at the condition where the operating line intersects the straight line  $c/c_0 = q_m/q_0$ , because the breakthrough curve obtained in the range of the concentration higher than the plateau concentration cannot be extrapolated up to the level of a concentration lower than that. Further, as the width of a plateau zone on the breakthrough curve increases, the amount of hydrogen absorption at the breakthrough point decreases.

## Conclusion

An experimental investigation of the effect of plateau pressures on breakthrough curves of hydrogen was made using yttrium particle beds. The experimental curves were in good agreement with the numerical ones on the basis of the moving boundary in particles.

### Appendix 1 Equilibrium isotherm of yttrium

The equilibrium isotherm of yttrium was obtained by fitting the following equations to the experimental PCT data<sup>9)</sup>:

$$\frac{p_i}{p_{\text{plat}}} = \left( \frac{q_i}{q_l} \right)^{1/n} \quad q_i < q_l \quad (\text{A-1})$$

$$p_i = \exp \left( \frac{A + Bq_i}{R_g T} \right) \quad q_i \geq q_l \quad (\text{A-2})$$

The value of  $n$  in Eq. (A-1) is 0.5 for an ideal solid-solution phase. However, in many metal-hydrogen systems the  $n$  value is often different from 0.5. The value of  $B$  in Eq. (A-2) is 0 in a two-phase region while in a hydride phase the values of  $A$  and  $B$  become a function of temperature. The physical implication of Eq. (A-2) is that the relative partial molar enthalpies and entropies per mole of hydrogen are in proportion to the hydrogen uptake in the hydride. The values of  $n$ ,  $A$  and  $B$  are summarized in Table A-1, where the units of  $p_i$  and  $q_i$  are [atmospheres] and [H/Y] respectively. The values of the lower and upper limits in the two-phase region,  $q_l$  and  $q_u$ , which are read from the phase diagram of the yttrium-hydrogen system<sup>4)</sup>, are tabulated in Table A-2 as a function of temperature.

A comparison between the calculated isotherm and PCT data<sup>9)</sup> is shown in Fig. A-1.

### Appendix 2 Mass transfer data used for a comparison between numerical curves and experimental results

- (1) Fluid-film mass transfer coefficient,  $k_f$

The  $k_f$  value was estimated by the equation<sup>7)</sup>:

$$Sh = 2 + 1.1 Re^{0.6} Sc^{0.33} \quad (\text{A-3})$$

- (2) Solid-phase mass transfer coefficient,  $k_s$  and reaction rate constant,  $k_r$

The capacity coefficient of solid-phase mass transfer defined on the basis of the diffusion coefficient in the hydride phase and the reaction rate constant in the hydride phase were obtained by a comparison between calculated and experimental results. Their dependence on the column temperature, the fluid velocity and the hydrogen concentration were discussed elsewhere<sup>2)</sup>. The  $k_r$  value in the solid-solution phase was also obtained from comparing numerical results with the experimental ones. The diffusion co-

Table A-1. Values of  $n$ ,  $A$  and  $B$  for yttrium

$q_i < q_l$	$n$	$1/3$
$q_l \leq q_i \leq q_u$	$A$	$-54.3 \times 10^3 + 34.9T$
	$B$	0
$q_u < q_i \leq 1.75$	$A$	$(-54.3 + 16.0q_u) \times 10^3 + (34.9 - 18.0q_u)T$
	$B$	0
$1.75 < q_i < 2$	$A$	$8a_1 - 7a_2$
	$B$	$4a_2 - 4a_1$
$a_1 = \{-54.3 - 16.0(1.75 - q_u)\} \times 10^3 + \{34.9 + 18.0(1.75 - q_u)\}T$		
$a_2 = -19.7 \times 10^3 + 31.3T$		

Table A-2. Values of  $q_l$  and  $q_u$  for yttrium

$^{\circ}\text{C}$	$q_l$	$q_u$
400	0.37	1.65
500	0.43	1.54
600	0.47	1.40
700	0.49	1.25
800	0.52	1.12
900	0.54	1.04

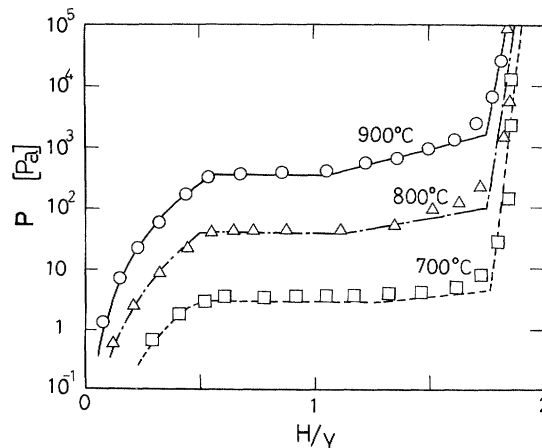


Fig. A-1. Comparison of calculated isotherm and experimental data<sup>9)</sup>

efficient in the solid-solution phase<sup>6)</sup> was used for the numerical calculations.

- (3) Axial dispersion coefficient,  $D_L$

The axial dispersion coefficient was estimated from an equation which comprises molecular diffusion and turbulent mixing<sup>5)</sup>:

$$D_L = \gamma_1 D_m + \gamma_2 \frac{ud_p}{\varepsilon} \quad (\text{A-4})$$

in which  $\gamma_2$  is a constant which normally has a value of 0.5<sup>5)</sup>. The bed tortuosity,  $1/\gamma_1$ , is related to the void fraction of the bed and mass transfer rates on particle surfaces and in solids<sup>8)</sup>. Since yttrium particles used in this experiment are not perfect spheres and the effect of phase transition in the particles should be also taken into consideration, the exact value of  $\gamma_1$  was not available prior to the experiments. Therefore, the reference value of  $\gamma_1$  was obtained from fitting the numerical curves to experimental results. The evaluated value was 2.0 under these experimental conditions.

## Nomenclature

$A$	= constant	[J/mol]
$B$	= constant	[J/mol]
$c$	= gas-phase concentration of hydrogen	[mol/m <sup>3</sup> ]
$D_m$	= molecular diffusion coefficient	[m <sup>2</sup> /s]
$D_L$	= axial fluid dispersion coefficient	[m <sup>2</sup> /s]
$d_p$	= particle diameter	[m]
$k_r$	= reaction rate constant on metal surface	[1/s]
$k_f$	= mass transfer coefficient for fluid-phase diffusion	[m/s]
$k_s$	= mass transfer coefficient for solid-phase diffusion	[m/s]
$n$	= constant	[—]
$p$	= hydrogen pressure	[Pa]
$q$	= solid-phase concentration of hydrogen	[—, H/Metal]
$R_g$	= gas law constant	[J/mol·K]
$Re$	= Reynolds number ( $=ud_p/\nu$ )	[—]
$Sc$	= Schmidt number ( $=\nu/D_m$ )	[—]
$Sh$	= Sherwood number ( $=k_f d_p/D_m$ )	[—]
$T$	= temperature	[K]
$u$	= superficial fluid velocity	[m/s]
$w_0$	= inlet molar fraction of hydrogen in fluid phase	[—]
$\gamma_k$	= constant defined by Eq. (A-4), $k=1, 2$	[—]
$\varepsilon$	= void fraction of bed	[—]
$\nu$	= kinematic viscosity	[m <sup>2</sup> /s]

## <Subscripts>

$f$	= fluid film
$i$	= interface

$l$	= lower limit
$m$	= mean
$plat$	= plateau
$r$	= reaction on surfaces
$s$	= solid phase
$u$	= upper limit
$0$	= inlet

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