Effect of PCT curve on the predicted thermal response and overall reaction rate in metal hydride tank

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Abstract: Heat and mass transfers in a packed bed of metal hydride particles are modeled considering reaction between the particles and hydrogen gas. The governing equations are numerically solved using control volume method. The experiments are also carried out using a cylindrical container with 50 mm I.D × 185 mm height. Particle diameter of metal hydride (MH) packed in the container is less than 100 µm. Water at a constant temperature flow through a jacket attached to the container wall. The absorption processes are operated under constant and variable pressures, while desorption processes are done at 338 K. The transient thermal response near the center of the container is measured using a thermocouple. The overall reaction rate is calculated from the hydrogen flow rate flowing from/to the container. Some models for PCT curve to describe the reaction rate of the MH have been proposed. In the numerical investigations, the effects of the PCT curve on the numerical results are investigated. As a result, the numerical transient temperature and reaction rate profiles strongly depend on the PCT curve. Selecting most suitable model, the numerical temperatures and reaction rates agree well with the experimental in the wide operation ranges.

Keywords: Hydrogen Storage, Simulation, Heat and mass transfer, PCT curve

1. INTRODUCTION

Metal hydride (MH) is attracting a lot of attention with a view to future hydrogen storage and transportation systems, heat pumps, actuators and so on. For these applications, packed bed reactors are usually utilized, to increase the solid–gas interface and promote the reaction. Since complicated phenomena such as chemical reaction, heat and mass transfer occur simultaneously in a reactor, many theoretical investigations for optimizing the reactor design have been carried out. Papers [1-3] are its example. Most of the past works investigated only heat transfer in the packed bed reactor. In these models, thermal equilibrium of the solid and gas phases and a uniform gas pressure were assumed. Jemni and Nasrallah [4] presented a model that takes into account the effects of the difference between solid and gas temperatures on the heat and mass transfer. Their approach would be more helpful for evaluating the dynamic behavior in a reactor. For the numerical simulation, it is important to know the relationship between the equilibrium pressure of the reaction, hydrogen composition in MH alloy and the temperature (what is called "PCT curve") since the difference between hydrogen pressure around MH and equilibrium pressure of MH is a driving force for the reaction. In the previous studies, \( P_{eq} \) for LaNi₅ have been approximated by a Van’t Hoff equation and a polynomial expression suggested by Nasrallah & Jemni [4]. However, both models couldn’t completely describe the experimental PCT data measured.

In this study, the effect of the PCT curve on the thermal response and reaction rate is investigated. Experiments are carried out under constant and variable hydrogen pressures. Absorption and desorption of hydrogen for LaNi₅ packed bed are investigated by comparing with the experimental and numerical results.

2. EXPERIMENTAL PROCEDURE

Figure 1 shows the schematic of the experimental apparatus. The system consists of a cylindrical packed bed reactor, a hydrogen reservoir, a thermostatic bath, a mass flow meter and a data collector. The geometry of the cylindrical reactor is 50 mm I.D × 185 mm height. MH particles are packed up to 70 mm height in the cylindrical reactor. LaNi₅ are used for MH alloy. The diameter of MH particles packed in the container is less than 100 µm. Water used as the heat transfer fluid is maintained at 293K by a thermostatic bath. Before each operation, the reactor is evacuated by a vacuum pump for several hours. After an evacuation is complete, absorption process is carried out supplying hydrogen with constant and variable pressures to the reactor through a mass flow meter. For the former operation, hydrogen is supplied from hydrogen bombe with a pressure regulator to maintain hydrogen pressure at 0.8

![Fig. 1 Schematic illustration of experimental setup](image-url)
MPa, while hydrogen previously stored in the reservoir at 0.8 MPa is supplied to the reactor for the latter operation. The volume of the reservoir is 10 L. After the absorption process, hydrogen desorption is carried out. The heat transfer fluid of which temperature is maintained at 338 K is provided to the reactor. Since MH is heated by the heat transfer fluid, hydrogen stored in MH is released and transported to the reservoir, which is evacuated before the desorption process, through the mass flow meter. Temperature of the reactor inlet gas and center of a packed bed are measured by a thermocouple. Reactor inlet pressures are measured by a pressure transmitter. The mass ratio of hydrogen to metal is calculated from the hydrogen mass flow rate.

3. MATHEMATICAL MODEL

A mathematical model considering heat and mass transfers for gas and solid phases are formulated and solved. A schematic illustration of the analytical region is shown in Fig. 2. An axial symmetry coordinate system (r-z axes) is used. The differences between the local gas and solid temperatures are considered [4]. The energy conservation equations of the gas (g) and solid (s) are given as

\[
\frac{\partial}{\partial t} (\rho g C_{pg} u_{g}) + \nabla \cdot (\rho g C_{pg} u_{g} T_{g}) = \nabla \cdot (\kappa g \nabla T_{g}) - h_{gs} S_{p} (T_{g} - T_{s}), \quad (1)
\]

and

\[
\frac{\partial}{\partial t} (\rho s C_{ps} u_{s}) + \nabla \cdot (\rho s C_{ps} u_{s} T_{s}) + h_{gs} S_{p} (T_{g} - T_{s}) = \frac{1}{1 - \varepsilon} \frac{dV}{dt}, \quad (2)
\]

The momentum conservation equation for the gas phase is considered as Darcy’s equation:

\[
\mathbf{u} = -\frac{K}{\mu} \nabla P, \quad (3)
\]

where \( K \) is the permeability of the packed bed of particles, and is given by Kozeny-Carman’s equation;

\[
K = \frac{1}{5} \frac{\varepsilon^3}{(1 - \varepsilon)^2} \frac{1}{S_{p}}, \quad (4)
\]

When the MH particles are assumed to be spherical, the specific surface area \( S_{p} \) in Eq. (4) is \( 6/\varepsilon_{w}^{2} \).

The mass conservation equations for the gas and solid phases are:

\[
\frac{\partial}{\partial t} (\rho g u_{g}) + \nabla \cdot (\rho g u_{g} \mathbf{u}) = -m, \quad (5)
\]

and

\[
\frac{\partial}{\partial t} (\rho s u_{s}) + \nabla \cdot (\rho s u_{s} \mathbf{u}) = m, \quad (6)
\]

where \( m \) is the hydrogen mass absorbed or desorbed per unit time and unit volume and given by

(1) for absorption process

\[
m = \frac{C_{ab}}{1 - \varepsilon} \exp \left( -\frac{E_{ab}}{RT} \right) \ln \left( \frac{P}{P_{eq}} \right) \left( \frac{H_{m}}{M} \right) - \left( \frac{H}{M} \right), \quad (7)
\]

and (2) for desorption process

\[
m = \frac{C_{de}}{1 - \varepsilon} \exp \left( -\frac{E_{de}}{RT} \right) \ln \left( \frac{P}{P_{eq}} \right) \left( \frac{H_{m}}{M} \right) - \left( \frac{H}{M} \right), \quad (8)
\]

where, parameters \( C_{ab} \), \( E_{ab} \), \( C_{de} \) and \( E_{de} \) are given by 59.187 [1/s], 21.18 [kJ/mol], 9.57 [1/s] and 15.473 [kJ/mol], respectively. \( H \) is a mass ratio of hydrogen to metal. As seen in eqs. (7) and (8), there are two driving forces for the reaction. One is the pressure difference between hydrogen pressure \( P \) and equilibrium pressure.
$P_{eq}$, the other is the difference between $(H/M)_{max}$ and H/M. In this study, we compared three models of $P_{eq}$ in Eqs. (7) and (8). The first one is Van’t Hoff’s equation, which has been generally used [5]. The second one is Nasrallah and Jemni’s equation [4]. This model is considered the effect of H/M on the entropy change of the reaction, and assumes PCT data as a 5th ordered polynomial form. The last one is given by the fitted value of the literature PCT data. As shown in Fig. 3, PCT curve is divided into three sections. The initial stage of reaction, the plateau region and the final stage of reaction are defined by stage I, II and III, respectively. The features of each model are summarized in Table 1. These three models of PCT lines at 313K are compared in Fig. 4.

Then assuming hydrogen to be an ideal gas,

$$\rho_v = \frac{n M_g}{V} = \frac{PM_g}{R_g T_g}$$  \hspace{1cm} (15)

Substitution of Eq. (15) into Eq. (7) under the assumption of an ideal gas yields

$$\varepsilon M_g \left( \frac{1}{R_g T_g} \frac{\partial P}{\partial t} + \frac{\varepsilon M_g P}{R_g T_g} \frac{\partial}{\partial T} \left( 1 - \frac{1}{1 - \varepsilon_{ini}} \right) \right)$$

$$- \frac{K}{v_k} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial P}{\partial r} \right) - \frac{K}{v_k} \frac{\partial^2 P}{\partial r^2} = -m$$  \hspace{1cm} (16)

$$\varepsilon = 1 - \left( 1 + E_p \nu \right) (1 - \varepsilon_{ini})$$  \hspace{1cm} (18)

where $E_p$, $\nu$ and $\varepsilon_{ini}$ are the expansion coefficient (0.24 for LaNi5), reacted fraction and the initial void fraction, respectively. The initial and boundary conditions are also shown in Fig. 2. For the boundary condition, the measured pressure and temperature at the reactor inlet are used. The overall heat transfer coefficient $U$ is calculated using Monrad and Pelton’s equation for an annular tube [6]. $\lambda_{eff}$ is obtained by Kunii and Smith’s equation [7]. The governing equations described above were numerically solved by the control volume method developed by Patanker [8]. The typical number of mesh points generated in the computational domain are $21 \times 21$ and the time step is 0.2 sec.

4. RESULTS AND DISCUSSION

4.1 Absorption process

Figure 5 shows time variations of the temperature at reactor center $T_c$ and H/M for absorption process with constant hydrogen pressures. At the initial stage of the reaction, $T_c$ dramatically increases then reaches a peak value of 336K. After that, $T_c$ still exhibits almost peak value until the reaction finishes. Finally, it decreases to 293K, which corresponds to the temperature of the heat transfer fluid. In this figure, we compare the numerical results with experimental ones. Calculations with the three PCT models in Fig. 5 exhibit similar tendency to each other. As shown in Fig. 4, the difference between Van’t Hoff’s eq. and others is the changes in $P_{eq}$ for both initial and final stages of the absorption. Since the large

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difference between H/M and (H/M)_{max} occurs at the initial stage of the absorption process, the reaction is so fast. Thus difference between three numerical results seems to be small at the initial stage of the reaction. For the final stage of the reaction, although the pressure difference doesn’t reach to zero for Van’t Hoff’s as shown in Fig. 4, reaction finishes due to saturation of hydrogen in MH alloy. Fortunately the reaction would proceed to saturated state under the constant hydrogen pressure. This implies that the difference between calculation results using the three PCT models would be small under constant pressures. However, when the hydrogen pressure is variable, the difference would be large.

To investigate the effect of hydrogen pressure supplied on the calculation, experiments are carried out with variable hydrogen pressures. Figure 6 shows the comparison inlet pressure profiles measured and PCT curves. As seen, supplying pressure gradually decreases with the progress of the reaction. When \( P \) corresponds to \( P_{eq} \) the reaction would stop. Figure 7 shows time variations of \( T_c \) and H/M for absorption process with variable hydrogen pressures. Here, calculations for \( T_0 = 293 \) K are also plotted in Fig. 7. From the figure, Van’t Hoff’s eq. doesn’t give reasonable predictions for both H/M and \( T_c \).

4.2 Desorption process

Figure 8 shows time variations of \( T_c \) and H/M. As shown, while H/M gradually decreases with time, \( T_c \) increases after decreasing to 274 K at initial stage of the reaction. Numerical results with the three PCT models are also shown. These results imply that it is required for the prediction to consider PCT curves.

5. CONCLUSION

In this study, we investigated the effect of PCT curve on the predicted thermal response and overall reaction rate in the MH packed bed. As a result, when the reaction proceeded to the saturated state, the numerical results
would be affected not by the PCT model but the hydrogen concentration in MH alloy. On the other hand, when the reaction stopped at the plateau region, the effect of PCT curve on the numerical result was considerable. Therefore, it is important for the prediction to consider PCT curves in the numerical simulations.

### NOMENCLATURE

- \( a \): Packed bed radius \([\text{m}]\)
- \( C_p \): Specific heat \([\text{J/(kg·K)}]\)
- \( C \): Constant in Eq.(7),(8) \([\text{m}]\)
- \( d_p \): Diameter of particle \([\text{m}]\)
- \( \varepsilon \): Porosity
- \( E \): Activation energy \([\text{J/mol}]\)
- \( E_p \): Expansion coefficient
- \( h \): Heat transfer coefficient \([\text{W/(m}^2\text{K)}]\)
- \( H/M \): Hydrogen to metal atomic ratio
- \( k \): Thermal conductivity \([\text{W/(m·K)}]\)
- \( K \): Permeability \([\text{m}^2]\)
- \( l \): Packed bed height \([\text{m}]\)
- \( \lambda_{\text{eff}} \): Effective thermal conductivity \([\text{W/(m·K)}]\)
- \( m \): Hydrogen mass absorbed or desorbed
- \( M \): Molecular weight \([\text{kg/mol}]\)
- \( \mu \): Viscosity \([\text{kg/(m·s)}]\)
- \( \nu \): Reacted fraction
- \( \nu_k \): Kinetic viscosity \([\text{m}^2/\text{s}]\)
- \( n \): Number of moles \([\text{mol}]\)
- \( P \): Pressure \([\text{Pa}]\)
- \( Q \): Reaction heat \([\text{J}]\)
- \( r \): Radial coordinate \([\text{m}]\)
- \( R_p \): gas constant \([\text{J/(mol·K)}]\)
- \( \rho \): Density \([\text{kg/m}^3]\)
- \( S_p \): Specific surface area \([1/\text{m}]\)
- \( T \): Temperature \([\text{K}]\)
- \( T_h \): Heat transfer fluid temperature \([\text{K}]\)
- \( t \): Time \([\text{s}]\)
- \( u \): Velocity \([\text{m/s}]\)
- \( U \): Overall heat transfer coefficient \([\text{W/(m}^2\text{K)}]\)
- \( V \): Volume \([\text{m}^3]\)
- \( Z \): Axial coordinate \([\text{m}]\)

### Subscripts

- ab: Absorption
- de: Desorption
- g: Gas
- s: Solid
- eq: Equilibrium
- ini: Initial

### REFERENCES

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