Numerical study of three-dimensional heat and mass transfer in a metal–hydrogen reactor

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Abstract:
Three dimensional heat and mass transfer in a metal-hydrogen reactor are numerically studied using the control-volume-based finite element method (CVFEM). The distributions of the temperature and the hydride density on the hydriding process is presented and discussed. The effects of dimensions reactor, imposed hydrogen pressure, inlet temperature and hydride thermal conductivity in the reaction kinetic are also determined.

Key words: Hydrogen storage, LaNi5 hydride, Heat and mass transfer

1. Introduction
Worldwide demand for energy is growing at an alarming rate causing the exhaustion of fossil fuel resources and serious environmental problems. Hydrogen is seen by many as key solution for these problems, enabling clean efficient production of power and heat from a range of primary and renewable energy sources.

Large-scale use of hydrogen energy requires advances in storage technologies. Consequently, many pathways of hydrogen storage have been developed such liquidification, gas compression and hydrides. The last technology received much research interest recently due to its safety and its compactness. In fact, the hydrides are used to develop a great number of industrial applications such as the compressors, the systems of cooling and heating, the electric batteries and the storage of hydrogen aboard vehicles. These various applications are based on the phenomena of absorption of hydrogen by the metal. Thus, a good design of these applications requires the control of the hydriding process in the metal bed and thus the good comprehension of the coupled phenomena of heat and mass transfer taking place during the hydrogen absorption.

Several studies on transient heat and mass transfer in the metal hydride bed have been presented [1-6] for detailed analysis of metal-hydride bed operations. Demircan and co-workers [7], Man Yeong Ha and co-workers [8], Ataer and co-workers [9] investigate various bed geometries on hydriding process in order to reduce the storage time. Dogan et al. [10] presented a mathematical model describing the absorption of hydrogen in a metal hydride bed sandwiched between two cooling regions and they studied the effect of two charge systems on filling time. It is found that hydrogen must be supplied radially from both sides for a rapid filling. Kikkinides et al. [11] searched to improve the design and the control of metal hydride beds by integrating a cooling medium model and introducing additional heat exchangers at a concentric inner tube and annular ring inside the tank. Optimization results indicate that the total storage time is significantly improved.

Excepting the study presented by Aldas et al. [12], the majority of studies [1-11] consider that heat and mass transfer in the metal hydride bed are two-dimensional. Therefore, the main purpose of this work is to study three-dimensional phenomena of heat and mass transfer in case of cubic metal-hydrogen reactor.
2. Mathematical model

The cubic reactor, considered in this paper, exchange heat through six faces at a constant temperature as shown in Fig.1. It is packed with particle powders of metal hydrides: LaNi5 alloys.

The solid particles react with hydrogen to produce the hydride. It is considered as a porous medium where macroscopic differential equations are obtained by taking the average of microscopic equations over a representative volume and using closing assumptions.
- The mathematical model is based on the following assumptions:
  - The dispersion term and the tortuosity term are modelled as diffusive fluxes,
  - The viscous dissipation and compression work are negligible,
  - The solid and fluid temperatures are essentially equal,
  - The ideal gas law holds in the gas phase,
  - Thermophysical properties are constant.

Considering these assumptions, energy equation and hydrogen mass balance can be written in the following vectored form:

\[
\hat{\partial} \left( \alpha_1 \Phi \right) + \nabla \cdot (\vec{J}_{\Phi}) = S_{\Phi}
\]

where \( \vec{J}_{\Phi} \) is the combined convection-diffusion flux:

\[
\vec{J}_{\Phi} = \vec{J}_{s}^{c} + \vec{J}_{s}^{d}, \quad \vec{J}_{s}^{c} = a_2 \vec{V} \Phi, \quad \vec{J}_{s}^{d} = -\Gamma_{\Phi} \nabla (\Phi)
\]

where \( \vec{V} \) is the fluid flow velocity vector.

The meanings of the different terms which are figured in Eq. (1) are given in Table 1.

<table>
<thead>
<tr>
<th>Equations</th>
<th>( \Phi )</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>( r_\phi )</th>
<th>( S_{\Phi} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuity for gas</td>
<td>( P )</td>
<td>( \frac{\epsilon M_g}{RT} )</td>
<td>0</td>
<td>( \frac{K}{v_g} )</td>
<td>-m</td>
</tr>
<tr>
<td>Continuity for solid</td>
<td>1</td>
<td>( (1-\epsilon)\rho_s )</td>
<td>0</td>
<td>0</td>
<td>m</td>
</tr>
<tr>
<td>Energy</td>
<td>( T )</td>
<td>( \rho_g C_{pg} + (1-\epsilon)\rho_s C_{ps} )</td>
<td>( \rho_g C_{pg} )</td>
<td>( \varepsilon \lambda_{pg} + (1-\epsilon)\lambda_{ps} )</td>
<td>( m \Delta H )</td>
</tr>
</tbody>
</table>

Table 1: Specific forms of the general conservation equation

2.1. Reaction kinetics

The hydrogen mass absorbed or desorbed, m, per unit time and unit volume is given by [13]:

For the hydriding case

\[
m = C_s \exp \left( \frac{-E_a}{R_s T} \right) \ln \left( \frac{P}{P_{eq}} \right) \rho_s \left( \frac{H_c}{M_c} \frac{H}{M} - \frac{H}{M} \right)
\]
For the dehydriding case

\[
\frac{-E_d}{R \frac{P}{T}} \exp \left( \frac{P - P_{eq}}{P_{eq} \frac{H}{M}} \right)
\]  

(4)

For the LaNi5–hydrogen system [13]

\[
\begin{align*}
C_d &= 9.57s^{-1} \quad Ed = 16.473 \text{ kJ/mol de H2} \\
C_s &= 59.187 s^{-1} \quad Ea = 21.179 \text{ kJ/mol de H2}
\end{align*}
\]

2.2. Equilibrium pressure

For the LaNi5–hydrogen system, the evolution of the equilibrium pressure is given as a function of temperature and the hydrogen-to-metal atomic ratio (H/M).

\[
P_{eq} = f \left( \frac{H}{M} \right) \exp \left( \frac{\Delta H^o}{R \left( \frac{T}{T_{ref}} - 1 \right)} \right)
\]

(5)

where \( f (H/M) \) is the equilibrium pressure at the reference temperature \( T_{ref} \). This function \( f (H/M) \) is given by fitting the experimental data.

2.3. Initial conditions

Initially, the temperature, the pressure and the hydride density in the reactor are assumed to be constant:

\[
\begin{align*}
T(x, y, z, 0) &= T_0 \\
P(x, y, z, 0) &= P_0 \\
\rho_s(x, y, z, 0) &= \rho_0 \\
V_g^+ &= V_g^- = 0, \quad V_g^+ = f(P)
\end{align*}
\]

(6) (7) (8) (9)

2.4. Boundaries hydrodynamic conditions

\[
\begin{align*}
\frac{\partial P(0, y, z, t)}{\partial x} &= 0 \\
\frac{\partial P(L_x, y, z, t)}{\partial x} &= 0 \\
\frac{\partial P(x, 0, z, t)}{\partial y} &= 0 \\
\frac{\partial P(x, L_y, z, t)}{\partial y} &= 0 \\
\frac{\partial P(x, y, 0, t)}{\partial z} &= 0 \\
\frac{\partial P(x, y, L_z, t)}{\partial z} &= 0
\end{align*}
\]

(10) (11) (12) (13) (14)

The face \( z=L_Z \) corresponds to the charge (absorption) or discharge (desorption) of hydrogen in the reactor. The pressure is supposed to be constant

\[
P(x, y, L_z, t) = P_0
\]

(15)
2.5. Boundaries thermal conditions

The heat flux continuity through the six faces (plans \(x=0, x=L_x, y=0, y=L_y\) and \(z=0\)), permits to write the following equations:

\[
-\lambda_e \frac{\partial T(0, y, z, t)}{\partial x} = -h(T(0, y, z, t) - T_f) \quad (16)
\]

\[
-\lambda_e \frac{\partial T(L_x, y, z)}{\partial x} = h(T(L_x, y, z, t) - T_f) \quad (17)
\]

\[
-\lambda_e \frac{\partial T(x, 0, z, t)}{\partial y} = -h(T(x, 0, z, t) - T_f) \quad (18)
\]

\[
-\lambda_e \frac{\partial T(x, y, 0, t)}{\partial z} = h(T(x, y, 0, t) - T_f) \quad (19)
\]

Where \(h\) is heat transfer coefficient between gas and solid and \(h_0\) is the transfer coefficient between solid/air sides.

3. Numerical method

The system of equations presented in the previous sections is solved numerically by the control-volume-based finite element method (CVFEM). This method has the advantage of using a conservative formulation, which allows an easy interpretation of the physical sizes. In addition, thanks to the use of grid in finite elements, it allows a very great flexibility in the type of geometry considered. For each calculation point, eight nodes are used. Six are situated in \((o, x, y)\) plan; the two other nodes are located at \(Z\) direction. The method consists of defining a grid of points within the calculated domain and then builds around each point a control domain \(V_c\) (Fig.1). The face of reactor situated at \((o, x, y)\) is first divided into three-node triangular elements (Fig.2). Then, element barycenters ‘\(g\)’ are connecting with edge midpoints ‘\(P\)’ and ‘\(M\)’ and two nodes located at \(Z\) direction as shown in Fig.2. This creates a control volume around each node in the finite element grid.

Figure 1: Spatial-discretisation
4. Results and discussion

4.1. Validity of the theoretical model

In order to validate the established model and the numerical method employed, our results are compared with the theoretical data of Askri et al. [13] in two-dimensional cylindrical configuration having the same volume.

According to the Fig. 3.a, the maximum temperature reached is the same one for the two geometrical configurations of the metal-hydrogen reactor; however the process of absorption is faster in the case of the cubic reactor: this is explained by the fact that the heat-transferring surface is larger in the case of the cubic geometry, of this fact the quantity of heat evacuated of the interior towards the outside of the metal-hydrogen system higher than that is evacuated in the case of a cylindrical system what accelerates the process of absorption (Fig. 3.b).

Figure 3: Comparison of the temperature (a) and the mass (b) evolution in the center of the reactor for two different geometrical configurations
4.2. Time-space evolution of the temperature and the hydride density

The volume of the reactor is 216 cm$^3$. It is immersed in a bath of water maintained at a constant temperature $T_f$. The pressure of hydrogen is kept constant. The conditions used to simulate the operation of the metal-hydrogen system are presented in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Absorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating fluid temperature $T_f$ (K)</td>
<td>313</td>
<td>313</td>
</tr>
<tr>
<td>Initial bed temperature $T_0$ (K)</td>
<td>293</td>
<td>293</td>
</tr>
<tr>
<td>Pression $P_0$ (bar)</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Effective thermal conductivity $\lambda_e$ (W/mK)</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>Permeability $K$ (m$^2$)</td>
<td>16E-12</td>
<td>16E-12</td>
</tr>
<tr>
<td>Porosity $\varepsilon$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 2: Thermophysical properties of materials and data used in computations

Fig. 4 shows the temperature evolution within the reactor at the selected times, $t = 60, 180, 300, 1800, 3600$ and $6000$ s. As absorption is exothermic, the temperature, inside the reactor, first increases and then decreases because of the decrease in reaction rate.

It is noticed that the temperature is lower on the level of the walls than inside and in particular on the level of the four corners due to the external fluid cooling. Fig. 5 shows the metal hydride density evolution within the reactor at the selected times mentioned above. At the beginning, the hydriding process takes place near the walls of the reactor where the absorption equilibrium pressure is important due to the decreasing of the temperature. Beyond $t=3600$s, the kinetics reaction decreases and the system offers toward an equilibrium state.
Figure 4: Time-space evolution of the temperature in the plan z=3cm
Figure 5: Time-space evolution of the hydride density in the plan z=3cm
4.3. Influence of the geometrical dimensions and the operating parameters

The total hydrogen mass is plotted as a function of time and this is for different ratios Lz/Lx and Ly/Lx (Fig. 6). The reactor volume, the amount of the hydride metal, the initial pressure, the physical characteristics, and the boundary conditions were kept constant during the simulation. It is noticed that the ratios Lz/Lx and Ly/Lx for which the reactor needs the longest time, to reach the equilibrium state, is equal to the unit. This result can be explained by the fact that the reactor surface that permits the exchange of the heat with the cooling fluid presents a minimum at Lz/Lx = Ly/Lx = 1.

The effect of the initial pressure P0, on the mass absorbed at constant volume of the reactor, is shown in Fig 7. It is observed that, when P0 increases the reactor temperature increases and the bed attains the equilibrium state and thus cooling the fluid temperature rapidly. This is justified by the fact that a high pressure leads to an important reaction rate and consequently to a large amount of heat and of mass absorbed.

The effect of heating fluid temperature $T_f$ on the mass and temperature is presented in Fig 8. It is observed that the time needed to attain equilibrium state is reduced and the final mass absorbed is increased when $T_f$ decreases.

Fig.9 presents the temporal evolution of the total mass absorbed, for different values of the effective thermal conductivity of the solid. It is noticed that increasing the value of this parameter accelerates the kinetics of the reaction. However, an increase of $\lambda_s$ more than 5 W/m.K did not significantly affect the time needed by the hydride system to reach the equilibrium state.
5. Conclusions

In this study hydrogen storage in metal hydride bed is numerically investigated by the CVFEM. Mathematical model includes complex heat and mass transfer take place during the hydriding process. Time-space evolution of the temperature and the hydride density are determined. A study of sensitivity of the temperature and mass of hydrogen absorbed were carried out. It is shown that the choice of the pressure of hydrogen imposed, of the temperature of the external fluid and the geometry of the reactor is very significant. The results also showed that the transfers are sensitive to the values of the effective thermal conductivity of the solid.

6. References