Numerical study of a magnesium hydride tank

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Abstract. Hydrogen storage in metal hydride tanks (MHT) is a very promising solution. Several experimental tanks, studied by different teams, have already proved the feasibility and the interesting performances of this solution. However, in much cases, an optimization of tank geometry is still needed in order to perform fast hydrogen loading. The development of efficient numerical tools is a key issue for MHT design and optimization. We propose a simple model representing a metal hydride tank exchanging its heat of reaction with a thermal fluid flow. In this model, the radial and axial discretisations have been decoupled by using Matlab\textsuperscript{\textregistered} one-dimensional tools. Calculations are compared to experimental results obtained in a previous study. A good agreement is found for the loading case. The discharging case shows some discrepancies, which are discussed in this paper.

Nomenclature

$A$ surface [m$^2$] $S$ heat source [W.m$^{-3}$]
$\alpha$ hydrogenation $T$ temperature [K]
$C_{P_{MgH_2}}$ specific capacity [J.kg$^{-1}$.K$^{-1}$] $V$ volume [m$^3$]
$\Delta H$ heat of reaction [J.mol$^{-1}$] \textit{Subscripts}
$\varepsilon$ porosity oil heat transfer fluid
$h$ convection coefficient [W.m$^{-2}$.K$^{-1}$] $MgH_2$ magnesium hydride
$\lambda$ thermal conductivity [W.m$^{-1}$.K$^{-1}$] rad radial
$M$ molar mass [kg.mol$^{-1}$] $ax$ axial
$\rho_{MgH_2}$ density [kg.m$^{-3}$] eff effective

1. Introduction

Hydrogen will probably play an important role as an energy vector in the near future. However, an efficient and safe mean of hydrogen storage is still needed. During the last decade, reversible storage solutions based on Metal Hydride (MH) were largely studied. Hydrogen absorption in metallic compounds is a highly exothermic reaction while hydrogen desorption is endothermic. To improve the energy efficiency of this storage solution, the heat of reaction (75 kJ.mol$^{-1}$ for MgH$_2$) released/consumed during the absorption/desorption phases can be exchanged with an other system.

Pfeifer and al. \cite{1} studied the thermal integration of a high temperature Proton Exchange Membrane (PEM) fuel cell (200 °C) with a Metal Hydride Tank (MHT). A thermal fluid flow is used to transfer the heat generated by the fuel cell to the MHT and to provide the energy needed by the desorption reaction. Heat pumps systems based on MHT were also largely investigated.
These systems allow to recover waste heat at medium temperature (100 °C) to produce heat at higher temperature. This kind of systems also allows cold production. There also are many integration possibilities of MHT in co-generation systems. Meng and al. [3] proposed a Combined Heat and Power (CHP) system using a medium temperature heat source from industrial waste heat and solar panels to produce electrical power and heat. All these studies clearly show the need of efficient simulation tools for MHT thermal integrated systems.

Considerable efforts have already been done for MH reactors modeling [4, 5, 6, 7, 8]. All these numerical works have shown that heat transfer management in the MHT is a key issue to improve (un)loading times. In most cases, complete 3 or 2 dimensional Computational Fluid Dynamic (CFD) models are used to represent the hydride tank behavior. Reducing model complexity is necessary to improve calculation time and to study thermal integration of MHT in co-generation systems.

We have developed a simple model implemented with the Matlab software for a cylindrical magnesium hydride ($MgH_2$) tank heated-up or cooled-down by a thermal fluid flow. The sorption reaction and thermal models of the reacting bed are coupled to a second domain representing the thermal fluid. Calculations are compared to experimental results.

### 2. Magnesium hydride tank

Calculations performed with this model were compared to experimental data obtained with a 10 kg magnesium hydride tank [9]. The model was developed from the characteristics of this experimental tank.

Magnesium hydride powders activated by ball-milling with additives exhibit fast reaction kinetics and high stability upon hydrogenation cycles [10, 11, 12]. To improve the thermal conductivity, these powders are compacted with Expanded Natural Graphite (Figure 1) [13, 14]. Kinetic models for absorption and desorption reactions and thermodynamic properties of these composites are given in reference [15]. Thermophysical properties of magnesium hydride composites are reported in Table 1.

### 3. Model description

Our model was developed in order to simulate the behavior of a magnesium hydride tank coupled to an external heat source by a thermal fluid flow. Cylindrical $MgH_2$ composites of 70 mm external radius ($R_e$) are stacked (Figure 2) in a stainless steel tank as presented in Figure 3. These composites are drilled by a 10 mm radius ($R_i$) hole in their center in order to improve hydrogen circulation inside the tank. Moreover, a free space ($e_g$) is maintained between each
composite by a stainless steel grid. A second steel cylinder surrounds the first one with a 7 mm inter space ($R_{oil}$). A heat transfer fluid ($Marlotherm®$ SH) is flowing between these two cylinders to provide the heat requested for hydrogen desorption and to extract the heat generated during the loading step. The dimensions of the composites and the tank are reported in Table 2. After a transition period equal to about 10 cycles, the hydrogen storage capacity of the tank and loading time have been found constant which indicates a good stability of the MgH$_2$ sorption properties.

3.1. Model assumptions
As already reported by Chaise and al. [15], the following assumptions can be made to simplify the mathematical model of the magnesium hydride domain:

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**Table 1.** Thermophysical properties of magnesium hydride compacted disks containing 10% Expanded Natural Graphite (ENG) and effective properties used in the model

| Property           | MgH$_2$ composites | Homogeneous domain |
|--------------------|--------------------|--------------------|
| $\rho_{MgH_2}$ ($kg.m^{-3}$) | 1087               | 972                |
| $C_{p_{MgH_2}}$ ($J.kg^{-1}.K^{-1}$) | 1545              | 1545              |
| $\varepsilon$     | 0.44               | 0.50              |
| $\lambda_{rad}$ ($W.m^{-1}.K^{-1}$) | 15.7               | 14.3              |
| $\lambda_{ax}$ ($W.m^{-1}.K^{-1}$) | 2                  | 2                  |

**Table 2.** Geometric dimensions of the composites and the tank

| Dimension | Value |
|-----------|-------|
| $R_i$ (mm) | 10    |
| $R_e$ (mm) | 70    |
| $R_{oil}$ (mm) | 7     |
| $e_p$ (mm) | 10    |
| $e_g$ (mm) | 1     |
| $H$ (mm)  | 800   |

**Figure 3.** Scheme of the MHT (left) and homogeneous model (right)
thermal equilibrium between solid and gas phases is assumed inside the porous media

- the flow of hydrogen is considered laminar
- radiative heat transfers are neglected
- impact of the hydrogen flow on the pressure distribution within the porous media can be neglected

The last assumption is validated since the N dimensionless parameter defined by Chaise and al. [16] satisfies the condition $N \ll 1$ in all the cases we studied. It means that in all these cases, we can neglect the non-uniformity of pressure due to pressure drops inside the composites.

The thermal fluid is incompressible and heat diffusion phenomena in the flow are neglected. Thermophysical properties of the thermal fluid are considered constant along the heat exchanger and are taken at average temperature. In the fluid domain the temperature is supposed to be constant in the radial direction except inside the boundary layer.

3.2. Geometric simplifications

At a given z position the temperature is supposed to be homogeneous along the external radius ($R_e$) of the composites, so the problem becomes axisymmetric. As presented in Table 1 the radial heat conductivity ($\lambda_{rad}$) of magnesium composites is around 8 times higher than the axial one ($\lambda_{ax}$), so axial heat diffusion can be neglected. Finally, the inner space of the tank can be considered as a homogeneous domain with effective properties, as shown in Figure 3. The radial thermal conductivity of the homogeneous domain is given by expression 1. This effective conductivity is defined as the average value of the thermal conductivity of the composites and of the thermal conductivity of the stainless steel grids located between each composites.

$$\lambda_{eff} = \lambda_{rad} \frac{1}{1 + \frac{\varepsilon_p}{\varepsilon_g}}$$

Porosity of the homogeneous domain is given by equation 2 as a function of the real dimensions of the composites. Properties of this homogeneous domain are given in Table 1.

$$\varepsilon_{eff} = \frac{\varepsilon_p + \varepsilon_g}{\varepsilon_p + \varepsilon_g} + \frac{R_i^2 \varepsilon_p}{R_i^2 (\varepsilon_p + \varepsilon_g)} \tag{2}$$

The effective density is an average value related to the density of bulk magnesium $\rho_{Mg}$ and to the porosity of the homogeneous domain:

$$\rho_{eff} = \rho_{Mg} (1 - \varepsilon_{eff}) \tag{3}$$

3.3. Mathematical model

The temperature distribution inside the magnesium hydride domain is given by the one dimensional heat equation:

$$\rho_{eff} C_p \frac{\partial T}{\partial t} = \lambda_{eff} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + S \tag{4}$$

The heat source term $S$ is calculated from the reaction rate $\frac{d\alpha}{dt}$ given by the absorption and desorption kinetic models [15].

$$S = \rho_{eff} \Delta H w_t \frac{d\alpha}{dt} \tag{5}$$

where $\Delta H$ is the enthalpy of hydrogenation reaction, $w_t$ the hydrogen weight capacity of the composites and $M_{H_2}$ the molar weight of hydrogen.
The following boundary conditions are applied to this domain:

- \( (\frac{dT}{dr})_{r=0} = 0 \)
- \( T_{r=R_e} = T_w \)

The wall temperature \( T_w \) is calculated from the energy balance in the thermal fluid domain. The heat flux \( \varphi \) at the interface between the two domains is calculated from the temperature field in the \( MgH_2 \) as expressed by equation 6.

\[
\varphi = -\lambda_{eff} \frac{\partial T}{\partial r}
\]  

The energy conservation in the thermal fluid domain can be expressed as follow:

\[
V \cdot \rho_{MgH_2} \cdot c_{p,MgH_2} \frac{\partial T}{\partial t} + V \cdot \rho_{MgH_2} \cdot c_{p,MgH_2} \cdot v \frac{\partial T}{\partial z} = \varphi \cdot A
\]  

Where \( V \) and \( A \) are respectively the volume and the surface of an element, \( v \) the fluid velocity and \( \varphi \) the heat flux transmitted from the hydride domain.

The Nusselt number is calculated from the Gnielinski equation, which makes use of the hydraulic diameter \( D_h \):

\[
Nu_{Dh} = \left( \frac{f}{8} \right) \left( Re_{Dh} - 1000 \right) Pr \frac{1 + 12.7 \left( \frac{f}{8} \right)^{0.64}}{Pr^{1.8} - 1}
\]

where \( Re \) and \( Pr \) are the Reynolds and Prandtl numbers, respectively. The friction coefficient \( f \) is calculated with the Petukhov equation:

\[
f = (0.790 \ln(Re_{Dh}) - 1.64)^{-2}
\]

In the case of a laminar flow, the Nusselt number is equal to 3.66. Then, the convective heat coefficient \( h \) between the thermal fluid and the tank wall is calculated by:

\[
h = \frac{Nu_{Dh}}{\lambda_{oil}}
\]

Finally the wall temperature \( T_w \) is deduced from the \( h \) coefficient and the thermal fluid temperature \( T_{oil} \):

\[
T_w = \frac{\varphi}{h} + T_{oil}
\]

The temperature \( T_w \) is then imposed as boundary condition on the hydride domain. Several iterations are needed to check the following criterion: \( |T_{w\text{current}} - T_{w\text{previous}}| < 0.1K \). Then, the next space step can be calculated and so on. The hydride domain is divided in \( M \) sub-domains in the radial direction and \( N \) sub-domains in the axial direction.

Pressure drops due to valves and filters before the hydrogen tank inlet/outlet and the thermal contact resistance between the composites and the tank wall were measured on the experimental setup. To obtain a good agreement with the numerical results, these experimental values were incorporated into the model. The thermal contact resistance is supposed to be the same whatever the tank geometry. The pressure drop before tank inlet/outlet depends on the studied system and has to be modified for each cases.
The conditions of temperature and oil flow applied during the experimental tests and used in the model are presented in Table 3.

Table 3. Experimental conditions applied to the model as boundary and initial conditions

|                | Oil flow (NL.min⁻¹) | Inlet oil temperature (°C) | Initial temperature (°C) |
|----------------|---------------------|----------------------------|--------------------------|
| Loading        | 40                  | 244                        | 244                      |
| Discharging    | 30                  | 344                        | 344                      |

Figure 4. Absorbed hydrogen volume measured (straight line) and calculated (dashed line) during the loading stage

Figure 5. Desorbed hydrogen volume measured (straight line) and calculated (dashed line) during the discharging stage

4. Results and discussion
The conditions of temperature and oil flow applied during the experimental tests and used in the model are presented in Table 3.

Experimental and numerical results obtained for loading and discharging tests are compared in Figure 4 and 5, respectively. This model shows a good agreement with the real behavior of the magnesium hydride tank during the absorption reaction. It allows to predict the loading time satisfactorily.

However, for the desorption case, numerical results do not match the experimental results as well. The predicted discharging time is shorter than in the real case. Within the discharging experimental conditions, the N parameter defined by Chaise and al. [16] is equal to 0.2. In this special case, the hydrogen flow inside the magnesium hydride composites probably has a slight impact on the tank performances. Whereas, in our model the pressure and, thus, the equilibrium temperature are constant in all the hydride domain.

Hydrogenation and temperature fields calculated at mid-term loading are presented in Figure 6 and 7 respectively. As already observed in previous studies, the hydrogenation is moving as a front of reaction from the external radius $R_e$ to the center of the tank. Despite the large thermal conductivity improvement obtained by a high ENG content, heat exchanges remain the limiting phenomenon. In this case, the isothermal profiles are strictly parallel to the tank wall, so the problem can be represented by a one-dimensional model. A criterion to check when this simplification can be made will be presented in a next paper.

5. Conclusion
A simple model implemented with the Matlab software was developed to simulate the behavior of a metal hydride tank exchanging the heat of sorption reactions with a thermal fluid. Calculations were compared with experimental results obtained on a large scale magnesium hydride tank presented in a previous study. Experimental and numerical results are in good agreement, so
the assumptions we made match well with the reality. Experimental data of composites thermal conductivity and thermal contact resistance between the composites and the tank wall are also confirmed by the calculations. These results should be useful for the design of further metal hydride tanks and for the development of new models predicting the thermal integration of MHT into co-generation systems.

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