Finite element-based simulation of a metal hydride-based hydrogen storage tank

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1. Introduction

Storage is a key factor in the development of a hydrogen economy, in particular for the transport sector [1]. “On-board” hydrogen storage requires a safety and efficient technology, compatible with vehicle requirements. Among different storage methodologies, the reversible sorption of hydrogen on metal hydrides appears to be particularly interesting [2]. AB5 intermetallic compounds and especially LaNi5 metal hydride, are considered very promising for these applications, due to a high storage volumetric density, and operating conditions of pressure and temperature compatible with fuel cells (T = 20–60 °C, p = 1–10 bar) [3]. A metal hydride-based hydrogen storage tank is more compact and safe in comparison with traditional pressurized tanks. The U.S. Department of Energy (DOE) has established, in the framework of DOE Hydrogen Program, some parameters that represent the technological targets for developing an efficient on-board hydrogen storage tank. Among these, the tank fill time, which is particularly restrictive, must be less than 10 min, considering a stored hydrogen mass of 5 kg [4]. For this reason, one of the most investigated subjects in literature is the development of tanks able to efficiently provide/remove thermal energy during the hydrogen charge/discharge. Several mathematical models for analyzing hydrogen absorption in metal hydride beds have been presented in recent years. Mayer et al. [5] developed a one-dimensional model which showed that heat and mass transfer are key factors affecting the reaction rate in the reactor. Successively, Jenni and Nasrallah [6] presented a model for the two-dimensional transient heat and mass transfer within a cylindrical reactor. The influence of some parameters (reactor radius, inlet pressure and temperature) on the dynamic reactor performance was determined. Moreover, it was demonstrated that convective heat transport through the hydride bed is negligible. Aldas et al. [7], extended the mathematical model of Jenni and Nasrallah to three dimensions, demonstrating that hydrogen flow significantly influences the temperature profile in the system. Nakawaga et al. [8] predicted the transient heat and mass transfer phenomena through the hydride bed by using a two-dimensional mathematical model.
with hydriding and dehydriding kinetics. Validity of the local thermal equilibrium (LTE) assumption was demonstrated. Ha et al. [9] investigated the physical mechanisms occurring in the hydride bed by solving numerically a two-dimensional model. The authors emphasized the importance of improving the heat and mass transfer of the bed by increasing the thermal conductivity of the metal hydride particles and by inserting fins in the bed. Marty et al. [10] presented a two- and three-dimensional numerical simulation for prediction of the characteristics of an industrial tank filled with hydrides. The comparison between 2D and 3D calculations showed that a three-dimensional tank geometry is necessary to properly design the tank. Kikkinides et al. [11] simulated a two-dimensional cylindrical reactor with two concentric annular beds both surrounded by cooling fluid. The reactor was directly modeled and solved numerically using the software package gPROMS. Simulations showed that improvement of the storage time can be obtained by optimizing the design and the control strategy of the cooling system. Nakaso et al. [12] carried out a two-dimensional simulation of a cross section of a metal hydride reactor with embedded filters and cooling tubes. Simulations were carried out using COMSOL Multiphysics commercial code. Among the assumptions made to simplify the treatment of the problem, Mohan et al. [18] neglected pressure drops within the bed and did not simulate the heat transfer fluid flowing through the inner cooling tubes. Notwithstanding the above mentioned limitations, results of simulations reiterated the importance of bed thickness as a major parameter controlling hydrogen absorption rate.

The aim of this paper is to present a three-dimensional tool for simulating a whole metal hydride-based hydrogen storage tank, consisting of a metal hydride bed, a cooling system and heat transfer fluid. Mathematical simulations have been achieved through the description of transient heat and mass transport phenomena by partial differential equations (PDEs), using the COMSOL Multiphysics simulation environment. The finite-element approach allows easy adaptation of the model to different reactor geometries, allowing accurate analysis and optimization of the design.

In the first part of the paper, the governing equations of the model and the pertinent boundaries and initial conditions are introduced. Afterwards, simulations of a cylindrical LaNi5-based reactor able to accumulate about 1 kg of hydrogen are presented. Dynamic performance of the storage tank is evaluated for three different configurations of the cooling system.
2. Mathematical model

The studied reactor is a cylindrical reservoir (external radius 0.1 m, length 0.5 m) filled with commercial LaNi5 grains and able to accumulate about 1 kg of hydrogen. Three different designs of the cooling system were simulated and are depicted in Fig. 1. The first “basic” design presents seven tubes, in which the cooling water flows, that are displaced in symmetrical position along the metal hydride bed. The second design presents twelve symmetrical inner tubes, allowing a higher heat transfer surface. The third reactor presents the same twelve-inner tube configuration and is additionally surrounded by a cooling jacket. For all configurations, hydrogen enters in the reactor axial direction.

The main assumptions considered in developing the model are the following:

- a) The media is in local thermal equilibrium (gas temperature is the same as solid temperature).
- b) The solid phase is isotropic and has a uniform porosity.
- c) The gas phase is ideal.
- d) Equilibrium gas pressure is calculated by the Van’t Hoff equation, neglecting hysteresis and plateau inclination of the real pressure/concentration isotherms.
- e) Thermal–physical properties are constant.
- f) The system is adiabatic (no loss/gain of heat to the ambient).

The governing equations consist of energy balances for the cooling fluid, heat exchanger metal, hydride bed, and mass balances for hydrogen diffusion. The model describes hydrogen diffusion through the hydride bed using Darcy’s law and taking into consideration the kinetics of the adsorption and desorption process. Moreover, the following additional equations have been considered:

In particular, Eq. (5) determines the gas density, considering the assumption (c). Eq. (6) is the well known Darcy’s law. Eq. (7) estimates the sorption bed permeability with the Kozeny–Carman law [21]. Eq. (8) describes the reaction kinetics, where the constant Ca depends on the type of hydride; the values of the activation energy E_a for the LaNi5–hydrogen system are reported in literature [22]. Eq. (9) calculates the equilibrium pressure using Van’t Hoff’s law; A and B coefficients depend on the hydride considered [23].

The initial and boundary conditions are the following:

\[
\begin{align*}
T_f &= T_m = T_s = T_0; \quad p = p_0; \quad \rho = f(p_0, T_0)
\end{align*}
\]

Fig. 1 – The three different designs of the cooling system simulated: a) “basic” seven inner tubes; b) twelve inner tubes; c) twelve inner tubes plus cooling jacket.
Boundary conditions:

\[ T_f|_{z=0} = T_{cool} \]

where \( T_{cool} \) denotes the inlet temperature of the cooling fluid.

\[-\lambda \frac{dT}{dr}|_{r=r_m} = h_w(T_m - T_s)\]

where \( h_w \) denotes the thermal resistance at the interface metal hydride (\( r_m = \) external radius of metal tubes)

\[ p|_{z=0} = p_{ext} \]

where \( p_{ext} > p_0 \) denotes the inlet hydrogen pressure.

The other boundary conditions related to thermal insulations or symmetry are not shown.

The mathematical simulations were achieved through the description of the transport phenomena by Partial Differential Equations (PDEs), numerically solved through the Finite Element Methods (FEMs), using a commercial software package COMSOL Multiphysics. The software solves energy (convection and conduction), mass (diffusion) and momentum (Darcy’s law) transport equations by the “chemical engineering” module. Some specific user-defined subroutines were implemented for the calculation of specific parameters such as the absorption rate, equilibrium pressure etc.

First, the geometry of the reactor and the mesh map, related to the calculation tolerance, are defined. Fig. 2 shows the 3D computational domains implemented. The first domain simulates the geometry of the above described “basic” seven inner tubes. The second domain describes the twelve-inner tubes design. The case with the cooling jacket is introduced by fixing a proper heat transfer wall boundary condition.

For each domain, three different sub-domains are defined: i) the porous metal hydride bed, ii) the metal tubes used as a heat exchanger, iii) the flowing cooling fluid (i.e. water). For reasons of symmetry and in order to reduce the calculation time, the computational domain simulates a half reactor.

For introducing the metal hydride and gas properties, the boundary conditions and initial values are assigned. The convergence of the solution determines temperature, pressure and metal hydride density distributions.

3. Results of simulations

Simulations were carried out, for the three configurations described above, assuming the common input data reported in Table 1. The simulated process is the filling phase, considering an inlet pressure of 8 bar. The inlet temperature of the cooling fluid is at 20 °C. The tank is considered initially at a temperature of 20 °C and a pressure of 1.5 bar.

Fig. 3a, b, c shows the three-dimensional distribution of the temperature at \( t = 1000 \) s for the three configurations simulated. For all cases, the heating of the hydride bed due to the exothermic process of hydrogen sorption is clearly shown. Moreover, it can be seen that the bed portion near the cooling

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>[Ref]</th>
</tr>
</thead>
<tbody>
<tr>
<td>External radius of the hydride bed</td>
<td>( R_e )</td>
<td>0.1 m</td>
<td>–</td>
</tr>
<tr>
<td>Length of the hydride bed</td>
<td>( L )</td>
<td>0.5 m</td>
<td>–</td>
</tr>
<tr>
<td>External radius of metal tubes</td>
<td>( r_m )</td>
<td>0.005 m</td>
<td>–</td>
</tr>
<tr>
<td>Velocity of the external cooling fluid</td>
<td>( v )</td>
<td>0.5 m s(^{-1})</td>
<td>–</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>( T_0 )</td>
<td>20 °C</td>
<td>–</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>( p_0 )</td>
<td>1.5 bar</td>
<td>–</td>
</tr>
<tr>
<td>Initial hydride density</td>
<td>( \rho_0 )</td>
<td>3200 kg m(^{-3})</td>
<td>–</td>
</tr>
<tr>
<td>Saturation hydride density</td>
<td>( \rho_{ss} )</td>
<td>3240 kg m(^{-3})</td>
<td>–</td>
</tr>
<tr>
<td>Porosity of the hydride bed</td>
<td>( \epsilon )</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>Hydride specific heat</td>
<td>( C_{ps} )</td>
<td>419 J kg(^{-1}) K(^{-1})</td>
<td>[7]</td>
</tr>
<tr>
<td>Hydride thermal conductivity</td>
<td>( k_{ps} )</td>
<td>1.2 W m(^{-1}) K(^{-1})</td>
<td>[6]</td>
</tr>
<tr>
<td>Sorption enthalpy</td>
<td>( \Delta H )</td>
<td>30800 J mol(^{-1})</td>
<td>[21]</td>
</tr>
<tr>
<td>Wall heat transfer coefficient at the interface heat exchanger - hydride</td>
<td>( h_{aw} )</td>
<td>1650 W m(^{-2}) K(^{-1})</td>
<td>[7]</td>
</tr>
<tr>
<td>Hydride powder particle size</td>
<td>( d_p )</td>
<td>28.3 μm</td>
<td>[12]</td>
</tr>
<tr>
<td>Hydrogen charge pressure</td>
<td>( p_{ext} )</td>
<td>8 bar</td>
<td>–</td>
</tr>
<tr>
<td>Temperature of cooling fluid</td>
<td>( T_{cool} )</td>
<td>20 °C</td>
<td>–</td>
</tr>
</tbody>
</table>
tubes and the cooling jacket (case “c”) has a lower temperature than the other zones. The axial gradient of temperature is due to the inter-particle mass transfer resistance of the metal hydride bed, which limits the diffusion of hydrogen through the reactor.

Fig. 3 – Reactor temperature distribution at a simulation time $t = 1000\,\text{s}$ for a) seven inner cooling tubes; b) twelve inner cooling tubes, c) twelve cooling tubes and cooling jacket.

Fig. 4a, b, c show slice distributions of the hydride temperature, pressure and density in the reactor section $z = 0.25\,\text{m}$, after 1000 s, for the three configurations.

Fig. 4a shows that, for the “basic” seven inner tube configuration, the outer area of the hydride bed reaches a maximum
temperature of 49.6 °C, while only the parts very close to the cooling tubes are efficiently cooled down. This indicates that this cooling system offers limited thermal efficiency. The pressure after 1000 s reaches the value of about 4.5 bar, that is less than the inlet pressure of hydrogen $p_{ext} = 8$ bar. The calculated hydride density is about $3230 \text{ kg m}^{-3}$, still far from the saturation density $\rho_{ss} = 3240 \text{ kg m}^{-3}$, showing that, after 1000 s, the reactor has not yet completed the charge phase of hydrogen. The slice distribution of the hydride temperature for the twelve-inner tube configuration presented in Fig. 4b demonstrates a slightly improved cooling efficiency, as the maximum temperature reached by the hydride bed ($T_{\text{max}} = 47.75 ^\circ \text{C}$) is still rather high. Similarly to the previous case, the pressure and the density of the metal hydride bed are still far from the equilibrium conditions, indicating that the additional inner cooling tubes do not add a noticeable improvement of the reactor performance. On the contrary, Fig. 4c clearly demonstrates that the utilization of an external cooling jacket allows much higher cooling efficiency. Indeed, the slice distribution of the temperature shows that a large portion of the metal hydride bed is efficiently cooled down. The maximum temperature reached in the internal part of the bed is $T_{\text{max}} = 30.4 ^\circ \text{C}$, which is surely favorable for the hydrogen adsorption process. Indeed, the slice distribution of pressure and hydride density reach the quasi equilibrium values of 8 bar and 3240 kg m$^{-3}$, respectively.

Fig. 5 reports the profiles of hydride bed average temperature as a function of time for the three configurations simulated. All cases present similar dynamic behavior; The initial stage of the sorption process is characterized by a sharp increase in temperature due to the high amount of heat generated that can not be immediately dissipated by the cooling system. Afterwards, the temperature increases more gradually, until reaching the maximum average temperature, which is dependent on the specific configuration of the reactor (50 °C case “a”, 45 °C case “b”, 37 °C case “c”). Subsequently, the temperature slowly decreases approaching the temperature of the cooling fluid (20 °C). The time required to reach complete thermal equilibrium is rather long (20–40 min), depending on the cooling system configuration, due to the intrinsic low thermal conductivity of the hydride bed.

Average pressure evolutions are reported in Fig. 6, starting from an initial value of 1.5 bar to 8 bar, that is the inlet hydrogen pressure. Initially, the pressure increases rapidly due to the high reaction rate. Afterwards, the hydride saturates and the pressure increase approaching the inlet pressure.

Fig. 7 shows the comparison among transient profiles of the average hydride density which increases up to $3240 \text{ kg m}^{-3}$, in correspondence with the maximum hydrogen sorption capacity, about 1.3 wt%. The reactor with seven inner cooling tubes, which has the less thermally efficient configuration, completed the saturation reaction in about 25 min. This fill time is comparable with existing results in literature [7,11,24,25]. The reactor with twelve inner cooling tubes allows shorter fill time (20 min). Utilization of the external
cooling jacket allowed to further improve the performance of the reactor, which is able to complete the saturation reaction in about 15 min, which is rather close to the DOE’s target. Overall system weight was estimated to be about 70 kg. Gravimetric and volumetric capacities are 10 gH2/kgreactor and 40 gH2/lreactor, respectively. The above mentioned characteristics are in line with the features of some advanced metal hydride-based storage tanks presented in literature [26,27].

4. Influence of permeability and thermal conductivity of the metal hydride bed

Thermal conductivity and permeability of the metal hydride bed are key-parameters to improve the reactor performance [28]. Fig. 8 shows the time evolution of the average hydride density obtained for case “c” (twelve-inner cooling tubes and cooling jacket) with different values of hydride thermal conductivity.

As expected, an increase in thermal conductivity can be directly translated to a reduction of the reactor fill time. In particular, the favorable fill time of about 12 min was calculated when the metal hydride bed exhibits a thermal conductivity of 10 W m⁻¹K⁻¹. Further increase in thermal conductivity up to 15 W m⁻¹K⁻¹ does not indicate a significant improvement. Practically, promising results have been already obtained realizing absorbent beds, where the hydride is confined into highly conductive porous matrixes such as expanded graphite, metal foams, etc. [13,29]. Additional simulations were carried out for case “c”, in order to study the
influence of the metal hydride bed permeability. Results obtained are presented in Fig. 9, demonstrating that a permeability higher than $10^{-12}$ m$^2$ introduces severe mass transfer limitations affecting the dynamic efficiency of the reactor.

This indicates that research efforts should be addressed towards the realization of advanced sorbent beds, where the hydride is confined into highly conductive, and sufficiently permeable to hydrogen, matrixes.

5. Conclusions

In this paper, a Finite Element-Based model for simulating 3D metal hydride-based hydrogen storage tanks with different designs of the cooling system is presented. Simulation of a “base case” design, having seven inner cooling tubes, returned a reactor fill time of about 25 min, which is in line with existing literature results. Differently, simulation of a reactor with advanced cooling system design, consisting of twelve inner cooling tubes and an external cooling jacket, returned reactor fill time of about 15 min, which is close to the DOE’s target. Overall system weight was estimated to be about 70 kg. Gravimetric and volumetric capacities are 10 gH$_2$/kg$_{reactor}$ and 40 gH$_2$/l$_{reactor}$, respectively.

Further simulations demonstrated that the permeability and thermal conductivity of the hydride bed are crucial factors for an optimized tank design. In particular, the favorable fill time of about 12 min was calculated when the metal hydride...
Fig. 9 – Influence of the permeability on the saturation time for the case ‘c’ (twelve inner cooling tubes and cooling jacket).

This work has been financially supported by MIUR-FIRB Idee progettuali DM25768.

Acknowledgements

This work has been financially supported by MIUR-FIRB Idee progettuali DM25768.

References


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