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Optimization of hydrogen storage in metal-hydride tanks

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ABSTRACT

The storage time of hydrogen in metal-hydride tanks (MHTs for short) is strongly influenced by the rate at which heat can be removed from the reaction bed. In the present work a two-dimensional mathematical model is developed and validated against experimental results. This model is used, first, to evaluate the impact of the tank wall thermal mass on the hydriding process. Walls in steel and in brass are tested and the obtained results show that there is no significant effect on hydrogen storage time. Then, the established model is used to study the dynamic behaviour inside various designs of MHTs: i) a cylindrical tank, ii) a cylindrical tank with external fins, iii) a cylindrical tank with a concentric tube filled with flowing cooling fluid and iv) a cylindrical tank with a concentric tube equipped with fins. Optimization results indicate that almost 80% improvement of the storage time can be achieved over the case where the tank is not optimized.

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1. Introduction

Due to the depletion of fossil-fuel natural resources and the growing air-pollutant emissions produced by carbonaceous fuels, an alternative to these fuels is necessary. Hydrogen energy is the best solution due to its high calorific value and its environmental friendliness. However, the storage problem of hydrogen prevents its wide usage and commercialization. In recent years there has been increasing interest in using metal hydrides for hydrogen storage due to advantageous characteristics such as high volumetric density and better safety compared to conventional methods. Several numerical and experimental studies have been reported on heat and mass transfer in a metal-hydride bed. Gopal and Murthy [1] developed a one-dimensional heat transfer model based on the experiments carried out on a cylindrical metal-hydride reactor filled with $MmNi_{4.5}Al_{0.5}$. Shmalkov et al. [2] proposed a theoretical model of heat and mass transfer in metal hydride–hydrogen gas impurities systems. Their model makes it possible to describe the sorption processes taking into account the convective transfer in the metal-hydride modules, for gas mixtures containing impurities that are inactive or weakly active to the hydride-forming material. Jemni and Ben Nasrallah [3,4] developed two mathematical models, one based on separated solid and gaseous phases and the other considers solid and gaseous phases as a mixture. The effect of several parameters on the overall hydrogen storage efficiency was illustrated. Jemni et al. [5] presented an experimental approach to determine the reaction kinetics, equilibrium conditions and transport properties in $LaNi_5$–H_2 system. Heat and mass transfer effects were also determined experimentally. Based on Jemni and Ben Nasrallah's continuum mixture model, Mat and co-workers [6–8] carried out a detailed analysis and studied the parameters effecting the hydriding process, and extended the analysis to three-dimensional cases. Askri et al. [9] extended the previous studies [3,4] by investigating the effect of radiative heat transfer on sorption processes. Kaplan and Veziroglu [10] extended the work of Mat et al. [7] and

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Nomenclature

c_p	specific heat, $J\,kg^{-1}\,K^{-1}$
E_a	activation energy, $J\,mol^{-1}$
H/M	hydrogen-to-metal atomic ratio
h	heat transfer coefficient, $W\,m^{-2}\,K^{-1}$
m	hydrogen mass absorbed per unit time and unit volume, $kg\,s^{-1}\,m^{-3}$
P	pressure, Pa
r	radial space coordinate, m
R	reactor radius, m
R_g	gas constant, $J\,mol^{-1}\,K^{-1}$
T	temperature, K
t	time, s
z	axial space coordinate, m

Greek symbols

ΔH	reaction heat of formation, $J\,kg^{-1}$
ε	porosity
λ	thermal conductivity, $W\,m^{-1}\,K^{-1}$
ρ	density, $kg\,m^{-3}$
g_e	gas effective

Subscripts

a	absorption
e	effective
eq	equilibrium
g	gas
h	solid
hs	saturated

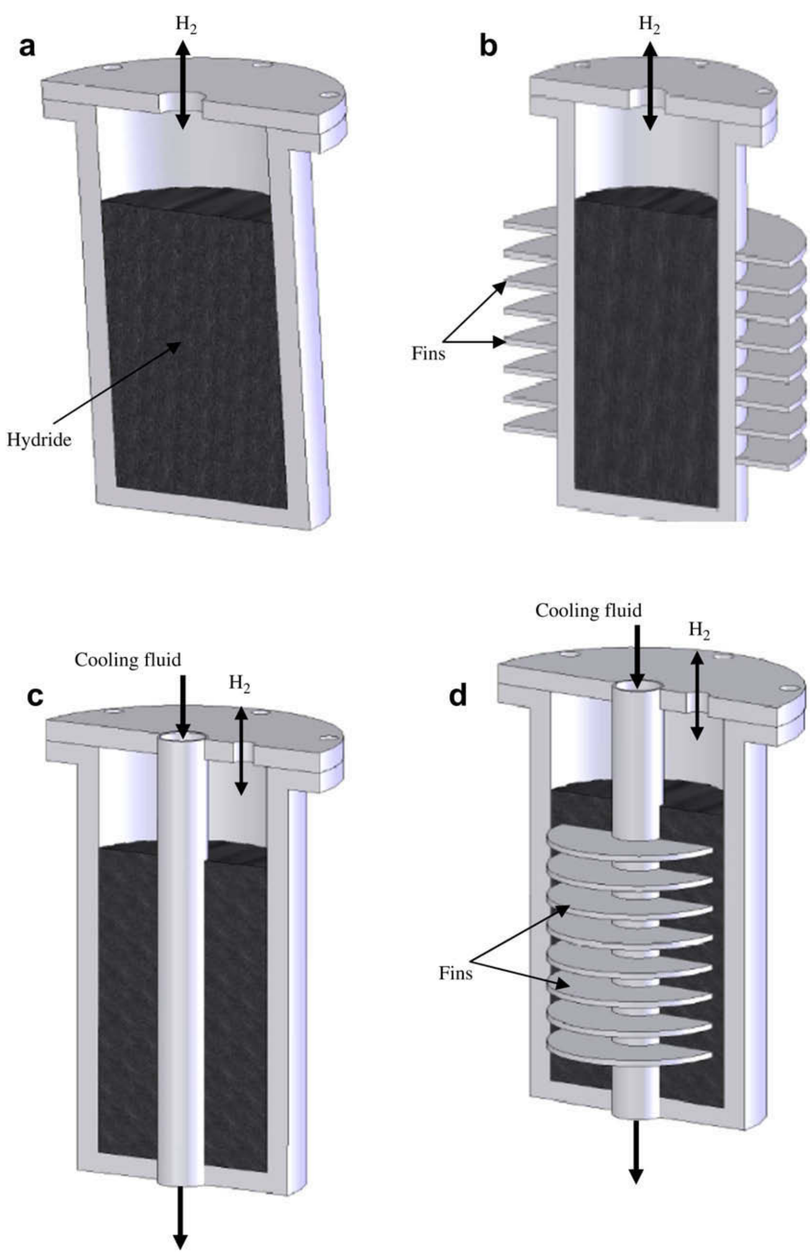

Fig. 1 – Schematic of MHTs used in simulations.

Table 1 – Specific forms of the general conservation equations.

Equations	Φ	f_Φ	Γ_Φ	S_Φ
Continuity for gas	1	$\varepsilon\rho_g$	0	$-m$
Continuity for hydride	1	$(1-\varepsilon)\rho_h$	0	m
Energy for hydride	T	$\varepsilon\rho_g c_{pg} + (1-\varepsilon)\rho_h c_{ph}$	$\varepsilon\lambda_g + (1-\varepsilon)\lambda_h$	$mT(c_{pg} - c_{ph}) + m\Delta H$
Energy for walls and fins	T	$\rho_f c_{pf}$	λ_f	0

Table 2 – The equilibrium pressure polynomial function coefficients.

Coefficients	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9
Absorption	0.0075	15.2935	−34.577	39.9926	−26.7998	11.0397	−2.8416	0.446	−0.0391	0.0014

investigated numerically the hydrogen storage process in a 2D metal-hydride bed including the full momentum balance equation, which is considered to be important when large pressure gradients exist in the system. Askri et al. [11,12] studied heat and mass transfer in a closed metal hydrogen reactor and in a reactor connected to a hydrogen tank. A formulation and numerical solution of non-local thermal equilibrium equations for multiple gas/solid porous metal-hydride reactors are presented by Lloyd et al. [13].

All these works confirmed the importance of heat transfer rate as a controlling parameter that determines the rate at which hydrogen gas can be stored in or extracted from an MHT. Also, these studies showed that the hydrogen sorption rate is high near the tank walls and established the importance of bed thickness as the major geometric parameter that influences the heat transfer rate. Thus, a number of works have investigated methods to increase heat transfer rates such as integration of copper wire net structure [14], insertion of nickel or aluminum foam [15,16], the micro-encapsulation [17], compacting metal-hydride powder with an expanded graphite [18], and integration of different heat exchangers [19–22]. Demircan et al. [19] studied numerically and experimentally two different MHTs. The first reactor is a cylindrical tank and the second consists of two concentric cylinders with the space between them used as a bed. Their results show that a bed geometry that provides more heat transfer area significantly reduces hydriding time. The effects of external convection on the thermodynamic behaviour in a metal-hydride tank have been studied by MacDonald and Rowe [20]. They showed that the addition of a large number of fins on the tank significantly impacts the discharge time. A simulation of a metal hydride–hydrogen storage device with embedded filters and cooling tubes is treated by Mohan et al. [21]. Results of the simulation confirm the importance of bed thickness as a major parameter controlling the rate of hydrogen absorption at all locations within the bed. They observed that the heat exchanger tube diameters have marginal influence on hydriding time at higher values. Mellouli et al. [22] experimentally examined the hydrogen sorption in an MHT equipped with an internal spiral

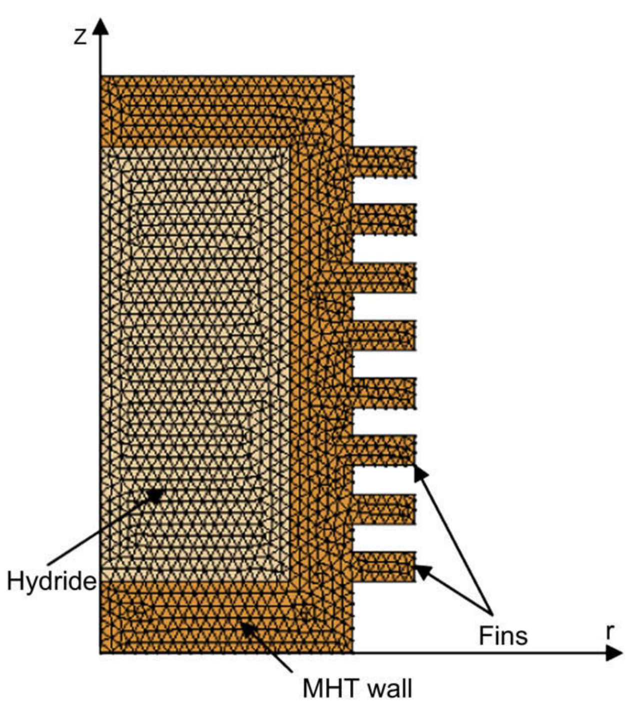

Fig. 2 – Unstructured mesh for case 2.

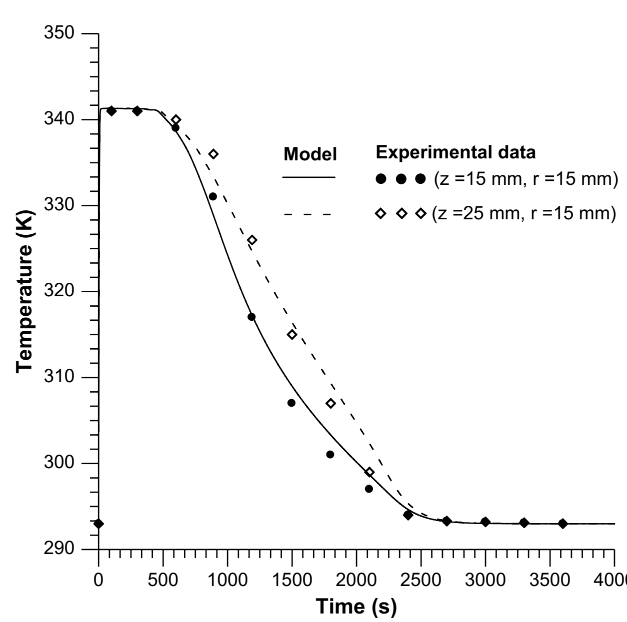

Fig. 3 – Comparison of prediction with experimental data.

Table 3 – Thermo-physical properties of steel and brass.

Parameter	Steel	Brass
Density (kg m^{-3})	7850	8400
Specific heat (J kg^{-1} K^{-1})	510	377
Conductivity (W m^{-1} K^{-1})	26	121

Table 4 – Parameter values used in computations.

Porosity	0.5
Initial bed temperature (K)	293
Cooling fluid temperature (K)	293
Inlet pressure of hydrogen (bar)	8
Effective thermal conductivity (W m^{-1} K^{-1})	1.32
Density of $LaNi_5$ (kg m^{-3})	8200
Specific heat of $LaNi_5$ (J kg^{-1} K^{-1})	530
Specific heat of hydrogen (J kg^{-1} K^{-1})	14,500

heat exchanger. They found that the charge/discharge times of the tank are considerably reduced.

In the present study, the effect of thermal mass of the tank wall on the hydriding process is evaluated. Furthermore, novel cooling design options are investigated by introducing a concentric heat exchanger tube equipped with fins and filled with flowing cooling fluid. The impacts of the proposed configuration on heat transfer rate and hydrogen storage time are studied and compared with other designs reported in the literature.

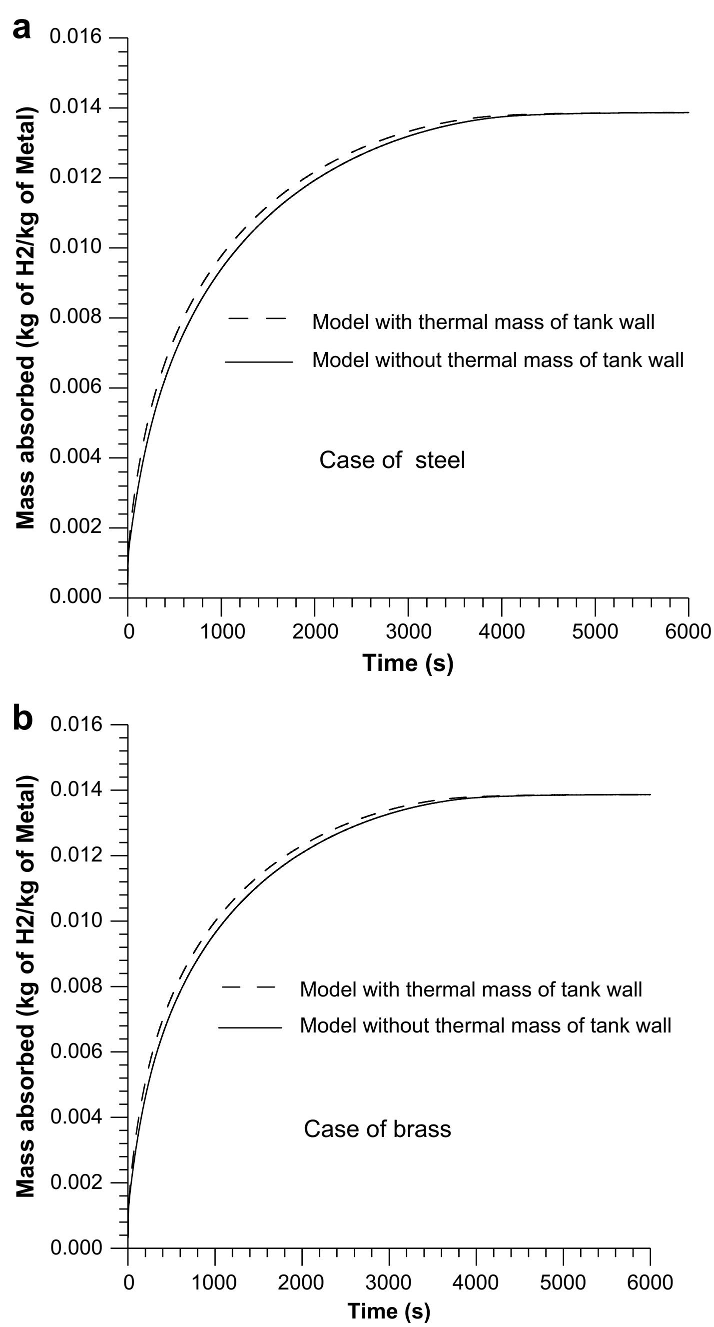

Fig. 4 – Effect of thermal mass of tank wall on hydrogen mass absorbed (case 1).

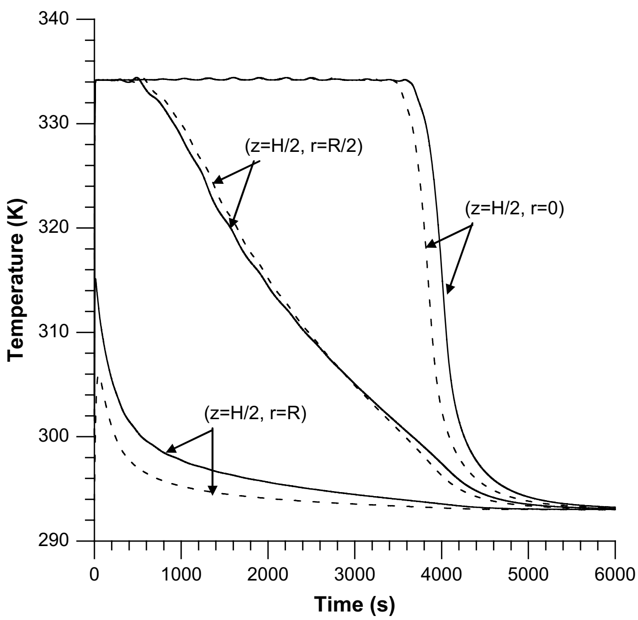

Fig. 5 – Effect of thermal mass of tank wall on temperature evolution (case 1). - - - - - model with thermal mass, — model without thermal mass.

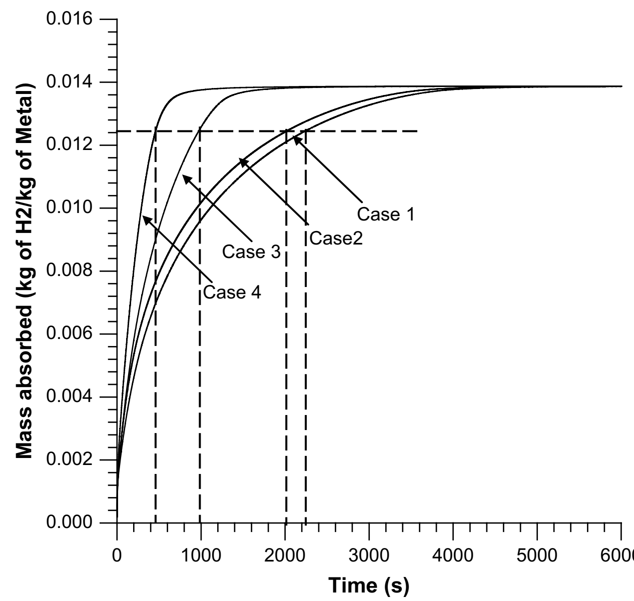

Fig. 7 – Time evolution of total H_2 mass stored for the different considered cases of MHT.

2. Mathematical model

The different MHTs examined in this work are presented in Fig. 1. The hydride material inside the tanks is assumed to have the properties of $LaNi_5$–H_2. Four designs are considered:

- Case 1: a cylindrical tank that exchanges heat through its lateral and base surfaces at a constant temperature (Fig. 1a).
- Case 2: a cylindrical tank equipped with fins on its lateral surface (Fig. 1b).
- Case 3: Similar to case 1, with the addition of a concentric heat exchanger tube without fins and filled with flowing cooling fluid (Fig. 1c).
- Case 4: Similar to case 1, with the addition of a concentric heat exchanger tube with fins and filled with flowing cooling fluid (Fig. 1d).

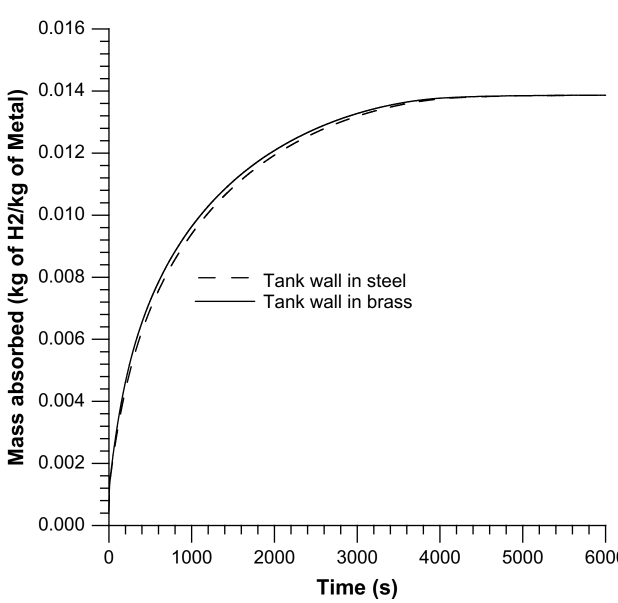

Fig. 6 – Effect of tank wall conductivity on hydrogen mass absorbed (case 1).

Being axisymmetric, the MHTs of Fig. 1 are modeled as a two-dimensional axisymmetric system. For the hydride powder, the macroscopic differential equations are obtained by taking the average of microscopic equations over a representative volume and using the following assumptions:

- Hydrogen is assumed as an ideal gas as the pressure within the bed is moderate.
- The local thermal equilibrium is valid.
- The radiative heat transfer is negligible.
- The advection transport term is negligible.
- Thermo-physical properties are considered independent of bed temperature and concentration.

Considering these assumptions, governing equations can be expressed in the following form [4]:

$$\frac{\partial}{\partial t}(f_\Phi \Phi) = \Gamma_\Phi \left[\frac{\partial^2 \Phi}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \Phi}{\partial r}\right)\right] + S_\Phi \quad (1)$$

The expressions of the different terms used in this equation are given for the hydride bed, MHT walls and fins in Table 1.

The hydrogen mass absorbed, m, per unit time and unit volume is given by [6]

$$m = C_a \exp\left(-\frac{E_a}{R_g T}\right)\ln\left(\frac{P}{P_{eq}}\right)(\rho_{hs} - \rho_h) \quad (2)$$

where C_a is a material-dependent constant ($C_a = 59.187\ s^{-1}$), E_a is the activation energy of the material ($E_a = 21.17$ kJ mol^{-1} of H_2), ρ_{hs} is the density of hydride at saturation.

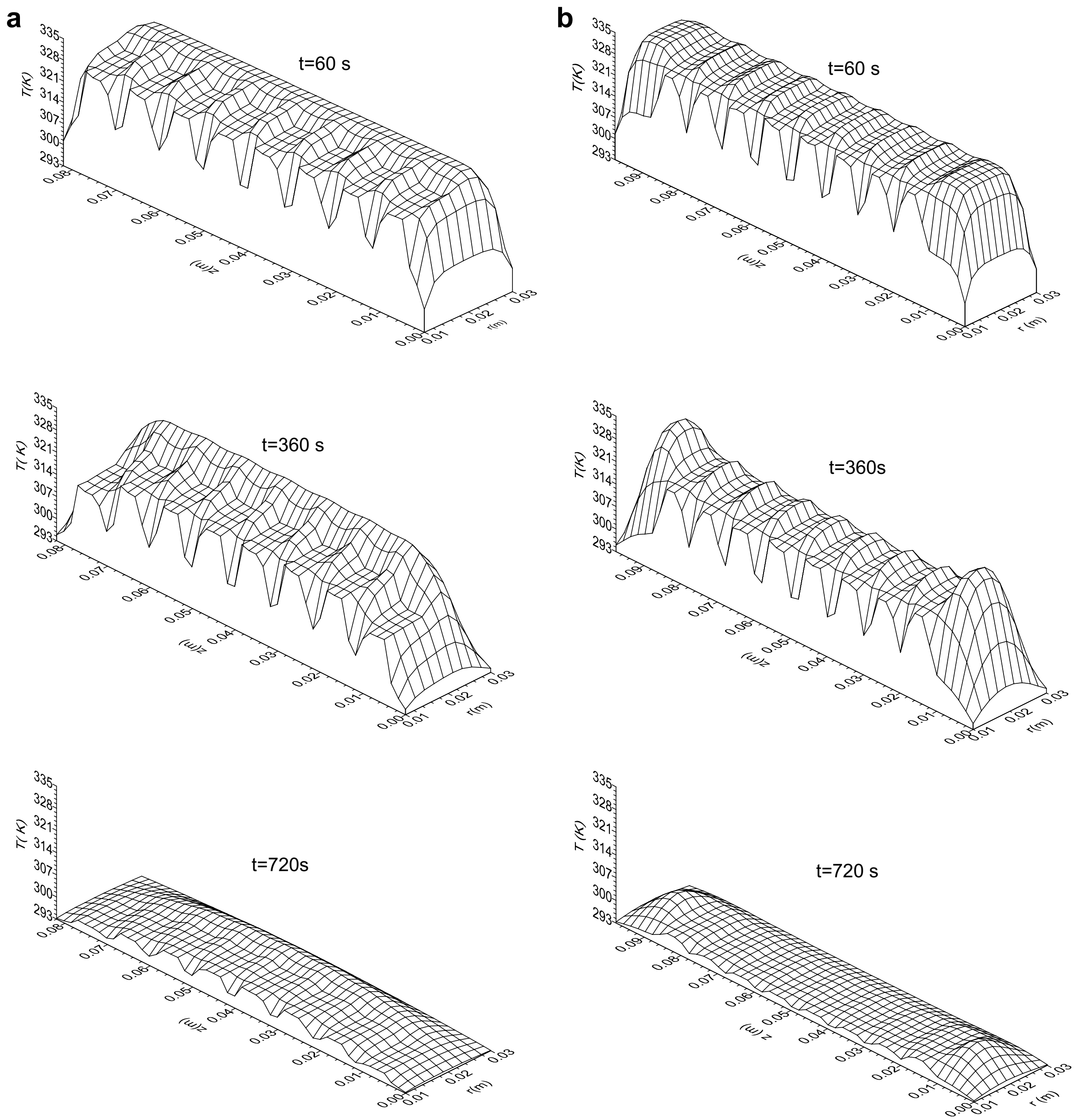

Fig. 8 – Temperature profile in the MHTs at selected times for case 4 (a: $D_{fins} = 0.02$ m, b: $D_{fins} = 0.025$ m).

The equilibrium pressure P_{eq} is given as a function of temperature and the hydrogen-to-metal atomic ratio (H/M).

$$P_{eq} = f\left(\frac{H}{M}\right)\exp\left(\frac{\Delta H}{R_g}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \tag{3}$$

where $f(H/M)$ is the equilibrium pressure at the reference temperature T_{ref}. This function $f(H/M)$ is a polynomial function of order 9, whose coefficients are given in Table 2 [5].

2.1. Initial and boundary conditions

Initially, the temperature and the hydride density in the MHTs are assumed to be uniform. Therefore,

$$T = T_0, \quad \rho_h = \rho_0 \tag{4}$$

■ Considering the symmetry condition about the z axis, then: For cases 1 and 2 (see Fig. 1a and b) we have

$$\left.\frac{\partial T}{\partial r}\right|_{(z,0,t)} = 0 \tag{5}$$

■ The heat flux continuity through the lateral area of the reactor, the lateral area of the concentric tube and the area of the fins permits to write the following condition:

$$-\lambda \mathrm{grad}(T) \cdot \vec{n} = h(T - T_f) \tag{6}$$

where $\vec{n}$ and λ represent, respectively, the thermal conductivity and a normal vector of the corresponding wall. T_f represents the ambient temperature for the lateral area of the tank and the cooling fluid temperature for the concentric exchanger.

If the thermal mass of the wall is taken into account, h denotes the convective heat transfer coefficient. Otherwise, it represents a thermal conductance between the hydride bed and the cooling fluid.

To simulate numerically the different MHTs considered in this work, the control volume finite element method (CVFEM) [12] was used to discretize the above-mentioned partial differential equations. Due to the geometric complexity of the calculation domains, a computer program was developed to generate unstructured mesh (Fig. 2). To solve the obtained algebraic system, a computer software was implemented in Fortran 90.

3. Results and discussion

In order to validate the established model, the numerical results are compared with the experimental data of Jemni et al. [5]. The calculated and the measured temperatures inside the reactor on two positions are plotted in Fig. 3. It is seen that numerical results agree satisfactorily with experimental data.

To study the effect of the tank wall thermal mass, the MHT of case 1 (Fig. 1a) is considered. The tank consists of a cylinder with an inner radius of 3 cm, an outer radius of 4 cm and an inner height of 8 cm. The thickness of the hydride bed is 6 cm. Steel and brass walls with the thermo-physical properties indicated in Table 3 are tested. The simulation is carried out for the parameter values given in Table 4.

For the model with thermal mass of MHT wall, the heat transfer within walls is analysed by solving the energy equation (Eq. (1)). For the model without thermal mass, heat transfer between hydride bed and cooling fluid is described by a thermal conductance.

The calculation results given by the two models are presented in Figs. 4 and 5. A small difference in the temperature profiles is observed essentially near the wall (Fig. 5) but it has no considerable effect on the hydrogen storage time (Fig. 4).

The model without thermal mass of MHT wall is used to evaluate the effect of the tank wall thermal conductivity on hydrogen absorption process. In spite of the large difference between the conductivities of steel and brass, Fig. 6 shows that the hydrogen storage time is nearly the same for the two metals. This result can be explained by the fact that heat transfer is controlled by the poor conductivity of the hydride powder.

To compare the considered cases (Fig. 1), the amount of hydride metal, the parameter values indicated in Table 4 and the boundary conditions were kept the same. As depicted in Fig. 7, the time required for 90% storage drops to about 2050 s, 980 s and 460 s in cases 2–4, respectively, representing a 10%, 56% and 80% improvement over the base case 1.

These results indicate that the integration of a concentric tube equipped with fins improves considerably the storage process.

To better understand the impacts of the integration of fins inside the hydride bed (case 4), the time space evolutions of temperature within the bed for two values of fins diameter ($D_{fins} = 0.02$ and 0.025 m) are plotted in Fig. 8. Keeping in mind that the absorption reaction is exothermic, the temperature inside the reactor first increases and then decreases. This is because of the decrease in reaction rate. From Fig. 8, it could be noticed that, near the concentric tube wall, the fins temperature is higher than the hydride temperature. Consequently, the temperature gradient between the cooling fluid/fins is higher than that between the cooling fluid/hydride. This result indicates that fins accelerate heat transfer from hydride to cooling fluid. After a substantial period of time, the metal tends towards saturation and the reaction velocity decreases. Consequently, the heat released from the bed becomes too weak and the temperature in the MHTs tends to the cooling fluid temperature.

A further step along this study was to examine if there is an optimal diameter of fins D_{fins} for case 4. Hence three different cases were compared, with $D_{fins} = 0.015$ m, 0.02 m and 0.025 m, while keeping constant the amount of hydride metal. The results (in terms of total H_2 stored and bed temperature) are shown in Figs. 9 and 10. It appears that the increase of fins diameter leads to an important reduction of storage time (Fig. 9).

In order to examine this result in a more systematic way, the time evolutions of temperature inside the fins and the hydride bed (along the line AB in Fig. 10a) are plotted for the three diameters. As shown in Fig. 10, by increasing fins diameter a faster heat transfer from hydride bed is obtained. Also, for the diameter values of 0.015 and 0.02 m the existence of a temperature maximum in the hydride region (Fig. 10b and c) is observed. This maximum shows that part of the heat is transferred from the hydride region to the fins and the other part is transferred to the external fluid through the lateral surface. From Fig. 10d ($D_{fins} = 0.025$ m) it is noticed that all of the heat generated in the hydride zone is transferred through the tank wall. This result indicates that the increase of fins diameter below this value has no important effect on absorption process.

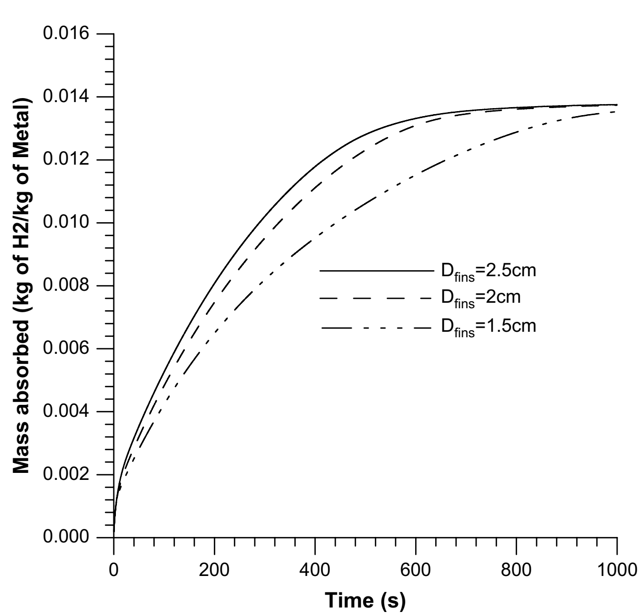

Fig. 9 – Time evolution of total H_2 mass stored for different values of diameter of fins (case 4).

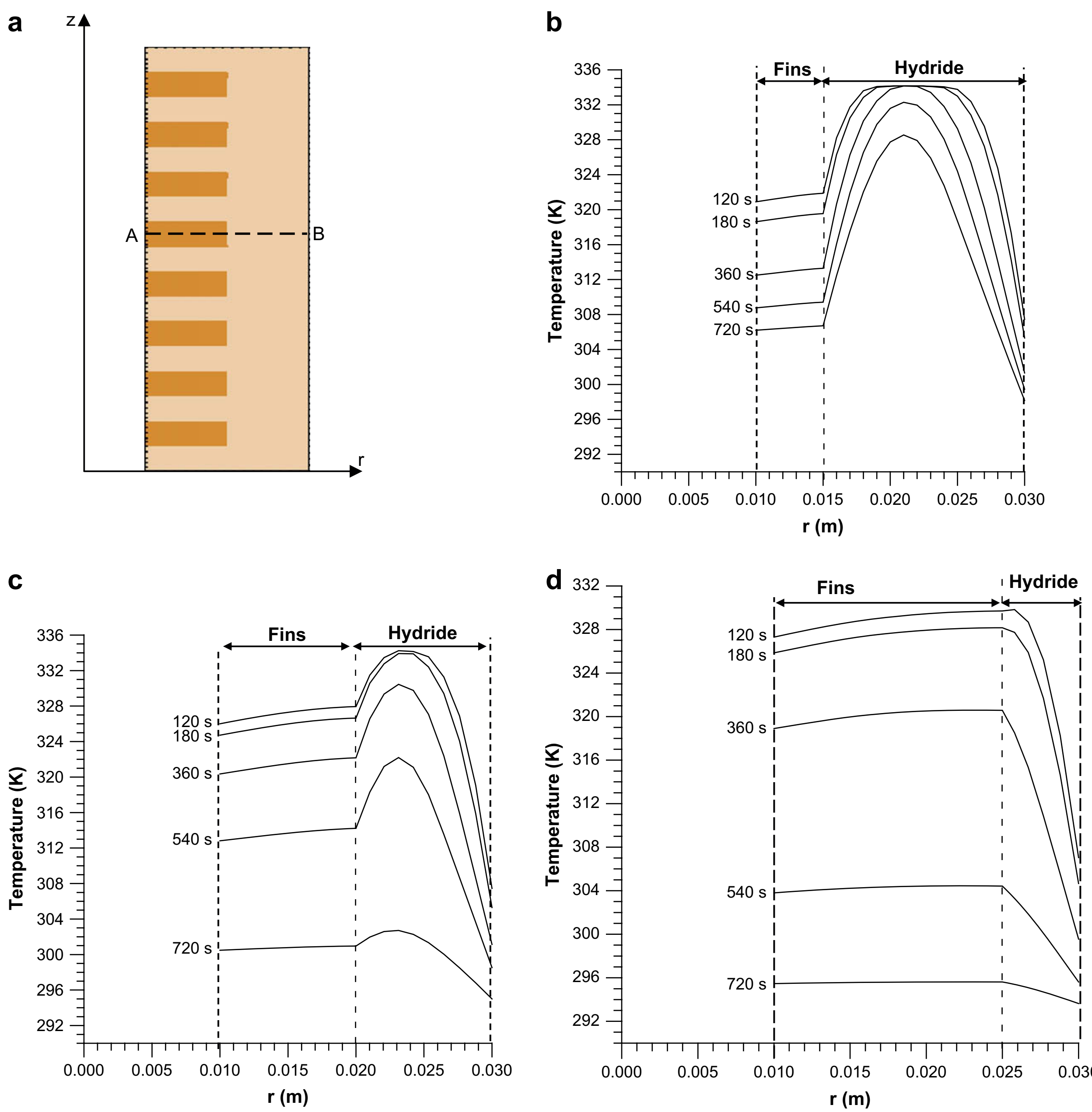

Fig. 10 – Effect of fins diameter on temperature evolution (case 4).

To examine the effect of thermal conductivity of fins that are integrated inside the hydride bed, fins in brass and in steel are considered. The time evolutions of hydrogen stored for the two types of fins are presented in Fig. 11. We noticed that a large value of thermal conductivity of fins has no important effect on storage time. This result can be justified by the poor conductivity of the hydride powder.

4. Conclusion

In this work, a 2D theoretical model describing hydrogen storage in metal-hydride tanks (MHTs) has been presented. Based on this model and the unstructured mesh, a computer program that simulates the behaviour of any arbitrarily shaped axisymmetric MHTs has been developed. The validity of the numerical model has been tested by comparison with experimental data and a good agreement is obtained. Then, the model was used to evaluate the impact of the tank wall thermal mass on the absorption process. Steel and brass walls were tested and the obtained results have shown that i) the tank wall thermal mass can be neglected and heat transfer between hydride powder and cooling fluid can be described by a thermal conductance, ii) the use of MHTs with a large wall conductivity has no significant effect on hydrogen storage time. In addition, the established model was used to study the dynamic behaviour inside various designs of MHTs and optimization results indicate that almost 80% improvement of the

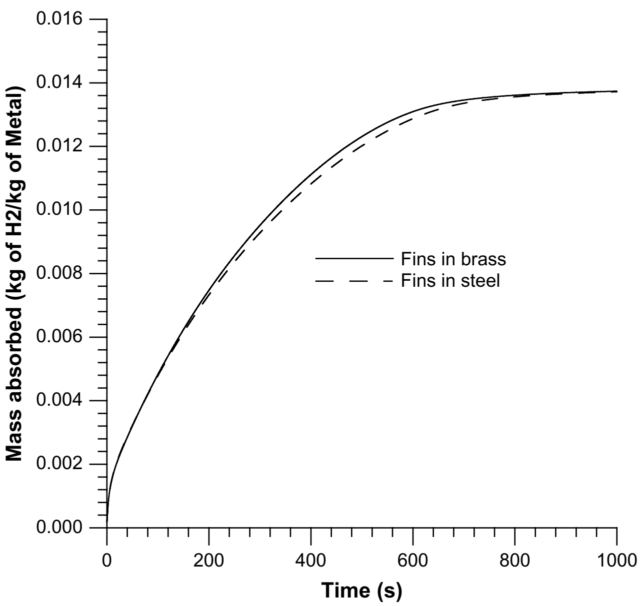

Fig. 11 – Effect of fins thermal conductivity on storage time (case 4).

storage time can be achieved when the design includes a concentric heat exchanger tube equipped with fins and filled with flowing cooling fluid.

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