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A simple criterion for estimating the effect of pressure gradients during hydrogen absorption in a hydride reactor

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ABSTRACT

Owing to the numerous coupled phenomena which occur during the loading with hydrogen of a metal hydride reactor, numerical simulations of such systems are very time consuming. Neglecting the fluid flow can reduce significantly the computing time, but it can lead to a wrong estimation of the hydriding time. This paper suggests a criterion which allows to quantify the error which is made when the fluid flow is neglected. It assumes conductive transfer controls the local evolution of hydridation in the reactor. Based on simple equations linking hydriding velocity to pressure and temperature, this study compares the solutions obtained with and without the gas flow. Using a finite volume numerical simulation, the validity of the criterion which is derived is checked on three classical tank geometries: it is shown that the criterion is independent of the tank geometry providing typical length scales can be defined for heat and gas diffusion. Finally, this criterion is successfully applied to an experimental magnesium hydride tank and its numerical modeling.

1. Introduction

Hydrogen is considered as a nice candidate for our future energy components. Because of its low mass density, its storage remains a challenge and many various solutions are considered. Among them, the storage based on the absorption principle is very promising under the condition that the weight capacities of the storing material are high enough. Recently, an active race to the development of new performing materials has started and quite fine results have been obtained on experimental reactors which have been shown to be able to store hydrogen in a reversible way [1,2]. Remarkable efforts have been made to improve the kinetics of absorption of the new hydrides which have been proposed. Nevertheless, for most materials, it appears that the absorption velocity is highly dependant of the heat transfer between the hydride powder and the external walls. Thus, the conception of a real industrially feasible tank needs a thorough account for this transfer. Considering the cost and the time which is needed for the construction of an experimental reactor, it is tempting to perform a preliminary numerical simulation to optimize the tank. The complete numerical prediction of the absorption or desorption of a gas in a metal hydride bed needs, in principle, to solve the full set of equations consisting of momentum and continuity equations together with the heat transfer equation. Nevertheless, the computation time can be very large when the geometry is that of an experimental laboratory or industrial prototype.

As a matter of fact, a "real" geometry (Fig. 1) is often rendered complex by many technical constraints. Concerning the tank, the necessity of preventing any gas leakage leads to design the walls and the lids of the tank with a thickness which prevents of neglecting them in the heat transfer calculation. As a consequence these walls should be meshed and will contribute to the weight of the computation. Furthermore, the complexity of the wall treatment is also rendered more complex by the circulation of a cooling fluid which aims at evacuating (or bringing) heat during the absorption (desorption) period. The associated fluid flow should also, in principle, be incorporated in the computation. Concerning the hydride bed, its poor thermal conductivity makes that additional heat transfer devices are often included inside the tank to enhance heat transfer [3]. For example, radial metallic fins can be used for enhancing the heat transfer between the core of the powder bed and the external walls. Again, this increases the computation time.

Many studies have proposed a mathematical modeling of the heat and mass transfer in the hydride reactor [4–14]. Some have tried to reduce the complexity of the system by investigating the importance of the main physical phenomena that occur during the hydriding process. Without experimental confrontation, Kuznetsov and Vafai [4] have established a set of criteria for the validity of local thermal equilibrium, steady-state and frontal model approximation with any kind of metal hydride. In a more pragmatic way and using a one-dimensional model, Choi and Mills [5]

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Nomenclature

α	hydride fraction ($0 < \alpha < 1$)
$\frac{d\alpha}{dt}$	hydriding velocity [s^{-1}]
C_a	kinetic coefficient [s^{-1}]
C_p	specific heat capacity [J/kg/K]
ε	porosity
E_a	activation energy [J/mol]
$F(\alpha)$	sorption mechanism function
ΔH°	molar enthalpy of reaction at standard conditions [J/mol]
ΔH	molar enthalpy of reaction in real conditions [J/mol]
K	permeability $\left(\vec{\nabla}P = \frac{\mu}{K}\cdot\vec{V}\right)$ [m^2]
λ	effective thermal conductivity [W/m K]
L_{heat}	typical heat diffusion length [m]
L_{gas}	typical gas diffusion length [m]
μ	dynamic viscosity of hydrogen [Pa s]
M	molar mass of hydrogen [kg/mol]
$P_{eq}(T)$	hydride equilibrium pressure [Pa]
P_{in}	inlet pressure of hydrogen [Pa]
P_0	reference pressure = 101.325 kPa
Pe	Peclet number = $Pe = \frac{V\cdot L_{gas}\cdot\rho_g\cdot C_{p_g}}{\lambda}$
ρ	density [kg/m^3]
R	universal gas constant = 8.314 JK^{-1} mol^{-1}
ΔS°	molar entropy of reaction at standard conditions [J/mol K]
T	temperature [K]
T_∞	cooling temperature of the vessel walls [K]
τ	loading time of the tank (s)
V	macroscopic gas velocity [m/s]
V_r	actual gas velocity between the metal particles ($V = \varepsilon\, V_r$) [m/s]
wt	maximum mass content of hydrogen in the metal [%]

Subscripts

s	simplified case where fluid flow is not taken into account
g	gas, hydrogen
m	bulk metal
kin	kinetic
por	porous
heat	heat transfer
gas	gas transfer

found an optimum bed size for heat pump applications. Gopal and Murthy [6] obtained good agreements between experiment and simulation that take into account pressure variations in the bed. Numerous 2D problems have been investigated concerning hydride beds and particularly for $LaNi_5$. Mat and Kaplan [7,8] obtained good agreement between experiment and simulation with only few assumptions. Jemni and Ben Nasrallah [9,10] have shown that using a single-phase-like model rather than considering the two different gas and solid phases does not affect the results. According to them, the effect of spatial pressure variation in the reactor is negligible under almost all conditions [11]. They also report that convection is insignificant on the hydriding rate: this seems opposite to Nakagawa et al. [12] who found that convection initially enhances the sorption process. Using a three-dimensional code, Aldas et al. [13] have revealed that neglecting the flow calculation in the computation only affects the temperature evolution in the reactor. The numerical simulation of a magnesium hydride tank has been achieved by Marty et al. [14].

The examination of the behavior of an absorption (or desorption) experiment shows that heat transfer controls the process. Actually there are two different periods: at the very beginning, the bed of hydrides is free of hydrogen and its temperature and equilibrium pressure are rather low. When hydrogen enters the tank, a sudden rise of the hydriding fraction occurs together with a violent increase in temperature in the entire bed. Following this very short period, typically lasting a few seconds, a long period arises during which the hydriding front slowly propagates from the colder towards the hotter regions [1]. The velocity of this front is controlled by the ability of the bed to remove the reaction heat which is generated by the absorption process. When computing such a phenomenon, it is then tempting to avoid the resolution of the momentum equations during this long period where the gas velocity is low and the time scale is large. Neglecting the velocity field has two consequences:

- The first is that the gas pressure will remain homogeneous during the whole calculation and the pressure variations which are generated by the flow of gas through the hydride porous bed will not be taken into account. This will lead to an overestimation of the gas pressure which features in the absorption velocity. In turn, this will lead to a possible error in the hydriding rate calculation.
- The second consequence is that the convective effect of the gas flow on the heat solution will be overlooked.

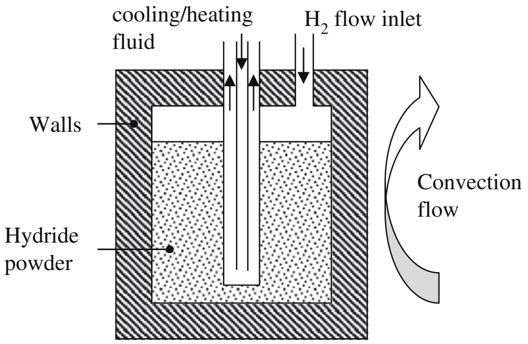

Fig. 1. Real hydride tank geometry.

This is the aim of this paper to assess the impact of neglecting the fluid flow in the prediction of the hydriding process. A dimensionless number will be proposed with the aim of estimating the error which is made when only heat conduction is considered inside the porous bed.

The paper is organized as follows: Section 2 details the construction of the dimensionless number which allows the assessment of the validity of the hypothesis consisting of neglecting the hydrogen flow. In this section, no particular geometry is assumed in such a way that it can be later applied to many different situations. Three types of classical geometries are discussed in Section 3: all these geometries are inspired from already published experimental works. Both planar and cylindrical geometries will be considered. The validity of the criterion which is proposed is tested in Section 4 on an experimental magnesium prototype which has been built in our laboratory.

2. Dimensionless analysis

In any metal hydride tank, heat from reaction has to be removed from or driven to the material. A privileged path for the heat diffu-

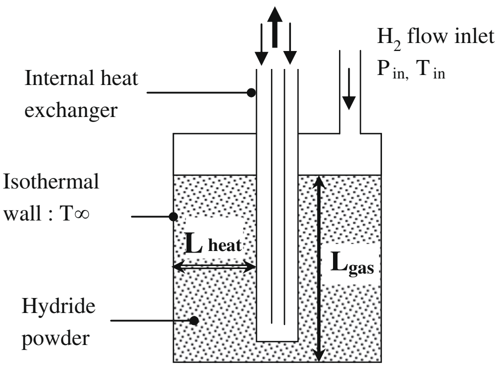

Fig. 2. Example of determination of the typical lengths for heat and gas diffusion.

sion can be then defined: let us call L_{heat} the associated length (Fig. 2). Similarly, a typical path for hydrogen diffusion can be defined: its averaged length will be denoted as L_{gas}. On the example shown in Fig. 2 hydrogen is fed at the top of the tank and has to penetrate vertically through the powder. The typical length L_{gas} is then the vertical height of the bed. In this figure, heat is removed either from the external wall or from an inner heat exchanger located near the tank axis. Consequently, the main path of the heat is radial and L_{heat} is equal to the radial thickness of the powder bed.

The aim of this section is to propose a criterion for assessing the importance of the fluid flow on the loading of a metal hydride reactor. The following assumptions will be made:

- Hydrogen in the hydride pores behaves as an ideal gas.
- Inter particle radiation heat transfer is neglected.
- The hydriding reaction is moving like a front inside the powder bed.
- Local gas temperature is the same than local solid temperature.
- The gas flow is laminar in the pores: $R_e = \frac{V_r \cdot \rho_g \cdot d_p}{\mu} \approx 1$ (d_p: diameter of porosity).

2.1. Governing equations

Four different phenomena have to be considered to evaluate the time of the reaction:

- The reaction kinetics, first, which links thermodynamics parameters to the rate of advancement of the hydriding reaction.
- The heat transfer equation which determines the temperature field in the tank as a function of the thermal properties of the bed, the fluid velocity and the reaction rate.
- The gas diffusion law which specifies the dependence between the velocity and the pressure field by the mean of the Darcy law.
- And finally, the thermodynamic property of the material which imposes a dependence between the equilibrium pressure and the temperature.

The exact expression of the kinetics of the reaction is dependant upon the material which is considered. For $LaNi_5$ for example, most of the experimental studies [2,9,15] agree with the following expression:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = C_a \cdot e^{\frac{-E_a}{RT}} \cdot \mathrm{Ln}\frac{P}{P_{eq}} \tag{1}$$

where, at first order, the hydriding velocity of the reaction is dependent on the difference between the gas pressure P inside the tank and the equilibrium pressure P_{eq} of the powder which is a function of temperature only. As discussed previously, the hydriding of the powder occurs on a hydriding front where the gas pressure is very close to the equilibrium pressure. A first order development of the last term of Eq. (1) allows to simplify this equation to:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_{kin} \cdot (P - P_{eq}) \tag{2}$$

where $K_{kin} = C_a \cdot \frac{e^{\frac{-E_a}{RT}}}{P_{eq}}$. Considering now the case of magnesium, [1,14] suggest an expression which, in addition to pressure and temperature, contains the hydriding fraction α itself:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = C_a \cdot e^{\frac{-E_a}{RT}} \cdot \frac{(P - P_{eq})}{P_{eq}} \cdot F(\alpha) \tag{3}$$

The function $F(\alpha)$ is tightly dependant upon the material behavior. This function reflects the phenomenon which limits absorption. Typically, this decreasing function varies from a high value at the very beginning of absorption ($\alpha = 0$), to zero when absorption is completed ($\alpha = 1$). Integrating this function from $\alpha = 0$ to $\alpha = 1$ gives 1. In order to obtain an explicit expression of the kinetics, we intentionally assume that $F(\alpha)$ is constant and equal to 1. Consequently, Eq. (3) can also be approximated under the form shown in Eq. (2). Then, from Eq. (2) we see that the absorption rate is proportional to the difference between the gas pressure and the equilibrium pressure independently of the type of metal hydride which is considered ($LaNi_5$ or magnesium).

The energy equation which links the temperature and the velocity fields contains also a source term which will be proportional to the hydriding rate of the reaction. Using the averaged formulation which is classically applied to such porous media gives:

$$\rho \cdot C_p \cdot \frac{\partial T}{\partial t} + \rho_g \cdot C_{p_g} \cdot \vec{V} \cdot \vec{\nabla} T \cdot = \lambda \cdot \nabla^2 T + S \tag{4}$$

where the source term S takes into account the exo/endothermic character of the sorption process and is defined as:

$$S = \frac{\mathrm{d}\alpha}{\mathrm{d}t} \cdot \mathrm{wt} \cdot \rho_m \cdot (1 - \varepsilon) \cdot \left(\frac{\Delta H}{M}\right)$$

Here ΔH is the molar enthalpy of reaction in real conditions, and $\rho \cdot C_p = \varepsilon \cdot \rho_g \cdot C_{p_g} + (1 - \varepsilon) \cdot \rho_m \cdot C_{p_m}$. This averaged formulation of the density and heat capacity is obviously rough but allows the simplifications which are necessary for the global analysis which is done here.

Convective heat transfer is actually weak compared to heat diffusion. That can be checked by calculating the Péclet number in the porous media: $Pe = \frac{V \cdot L_{gas} \cdot \rho_g \cdot C_{p_g}}{\lambda}$ which should be smaller than unity. Considering the magnesium experience which will be describes in Section 4 we find $Pe = 3.10^{-2}$ which is reasonably smaller than unity. In a cylindrical tank with a vertical axis, the existence of horizontal temperature gradients can also produce a natural convection flow. Estimating the order of magnitude of the resulting velocity shows that it is 10^7 times weaker than the velocity of the main absorption phenomenon. Consequently, natural convection will be omitted. Considering now a $LaNi_5$ facility such as that described in [2] produces a Peclet number of 0.1 which is also in reasonable agreement with the hypothesis stating that heat diffusion is the predominant mechanism of heat transfer in the powder. Eq. (4) now reduces to a transient heat conduction equation with a source term. The transient term quantifies the energy which is necessary to change the temperature inside the material. It is easy to show that this energy is negligible when compared to that which is produced by the reaction in the second period of the loading process. Another point of view for examining this question is to consider the time scale of the reaction which is much larger than the typical diffusion time which is roughly equal to $\frac{\rho \cdot C_p \cdot L_{heat}^2}{\lambda}$: this, again, shows that the governing phenomena during the hydriding of the tank is a balance between the production of heat via the source term and its diffusion through the powder bed and the walls of the container.

As a result, immediately after the end of the short period which corresponds to the fast heating of the tank when hydrogen first enters, the energy equation simplifies to:

$$\lambda \cdot \nabla^2 T + \frac{\mathrm{d}\alpha}{\mathrm{d}t} \cdot \mathrm{wt} \cdot \rho_\mathrm{m} \cdot (1-\varepsilon) \cdot \frac{\Delta H}{M} = 0 \tag{5}$$

Using L_heat as a typical length scale allows to approximate the Laplacian operator of Eq. (5) which now writes:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{T - T\infty}{K_\mathrm{heat}} \tag{6}$$

where the constant K_heat is defined as:

$$K_\mathrm{heat} = \frac{L_\mathrm{heat}^2 \cdot (1-\varepsilon) \cdot \mathrm{wt} \cdot \rho_\mathrm{m} \cdot \Delta H}{\lambda \cdot M}$$

From Eq. (6) we see that the absorption rate is proportional to the difference between the temperature of the walls which are thermally-controlled and the temperature of the porous bed.

Consider now the diffusion of the gas which is controlled by the Darcy law:

$$\vec{\nabla} P = \frac{\mu}{K} \cdot \vec{V} \tag{7}$$

The velocity field which appears in Eq. (7) is obtained from the mass conservation equation which writes:

$$div(\rho_\mathrm{g} \cdot \vec{V}) = \rho_\mathrm{m} \cdot wt \cdot (1-\varepsilon) \cdot \frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{8}$$

and where the time dependant term $\frac{\partial \rho_\mathrm{g}}{\partial t}$ has been omitted: this hypothesis is supported by the fact that the time-variation of the mass of gas which is present inside the tank is small compared to the mass of gas that diffuses through the porous medium to be absorbed. Then Eq. (8) simply expresses a balance between the incoming flux of gas and the absorption in the porous media. Using L_gas as a characteristic length for estimating the pressure gradient in Eq. (7) and the velocity gradient appearing at the left-hand side of Eq. (8) gives:

$$\rho_\mathrm{g} \cdot \frac{(P_\mathrm{in} - P)}{L_\mathrm{gas}^2} \cdot \frac{K}{\mu} = \rho_\mathrm{m} \cdot \mathrm{wt} \cdot (1-\varepsilon) \cdot \frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{9}$$

or, equivalently:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_\mathrm{por} \cdot (P_\mathrm{in} - P) \tag{10}$$

with $K_\mathrm{por} = \dfrac{\rho_\mathrm{g} \cdot K}{L_\mathrm{gas}^2 \cdot (1-\varepsilon) \cdot \mathrm{wt} \cdot \rho_\mathrm{m} \cdot \mu}$

Eq. (10) expresses the linear relation between the absorption rate and the pressure difference between the inlet gas pressure and the inner tank pressure. This equation is quite similar to Eqs. (2) and (6) which have been obtained previously.

Finally, as discussed earlier and according to the Van't Hoff law, the equilibrium pressure is only a function of temperature:

$$P_\mathrm{eq} = P_0 \cdot e^{\frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}} \tag{11}$$

2.2. Dimensionless number

We now aim at estimating the error which is done when the velocity field is not accounted for in the computation of the solution. The set of equations (2), (6), (10), and (11) will be used for this purpose. The pressure can be extracted either by subtracting Eq. (6) from (2):

$$P = \frac{(T - T_\infty)}{K_\mathrm{kin} \cdot K_\mathrm{heat}} + P_\mathrm{eq} \tag{12}$$

or by subtracting Eq. (10) from (6):

$$P = P_\mathrm{in} - \frac{(T - T_\infty)}{K_\mathrm{por} \cdot K_\mathrm{heat}} \tag{13}$$

Subtracting now Eq. (12) from (13) gives:

$$P_\mathrm{in} - P_\mathrm{eq}(T) - \frac{(T - T_\infty)}{K_\mathrm{por} \cdot K_\mathrm{heat}} = \frac{(T - T_\infty)}{K_\mathrm{kin} \cdot K_\mathrm{heat}} \tag{14}$$

Eq. (14) is a relatively simple equation which contains the temperature as its unique unknown. Let us introduce the so-called "simplified" case, denoted by the subscript "s" where the effects of the flow are neglected. The corresponding "simplified" solution for the pressure and temperature will be written P_S and T_S. This hypothesis is equivalent to neglecting the hydraulic resistance which is supported by the gas during its way through the powder ($K_\mathrm{por} \to \infty$). Under this hypothesis the gas pressure is homogeneous throughout the bed and $P_\mathrm{S} = P_\mathrm{in}$. Eq. (14) then writes:

$$P_\mathrm{in} - P_\mathrm{eq}(T_\mathrm{s}) = \frac{(T_\mathrm{s} - T_\infty)}{K_\mathrm{kin} \cdot K_\mathrm{heat}} \tag{15}$$

The simplified and the exact solutions are compared by subtracting Eq. (14) from (15):

$$P_\mathrm{eq}(T) - P_\mathrm{eq}(T_\mathrm{s}) + \frac{(T - T_\infty)}{K_\mathrm{por} \cdot K_\mathrm{heat}} = \frac{(T_\mathrm{s} - T)}{K_\mathrm{kin} \cdot K_\mathrm{heat}} \tag{16}$$

The temperature difference $T - T_\mathrm{s}$ represents the error on the hydride temperature when neglecting the effect of the hydrogen flow.

Assuming $T{-}T_\mathrm{s}$ to be sufficiently small and using Eq. (11) gives:

$$P_\mathrm{eq}(T) - P_\mathrm{eq}(T_\mathrm{s}) = (T - T_\mathrm{s}) \cdot \frac{\partial P_\mathrm{eq}}{\partial T}(T_\mathrm{s}) \tag{17}$$

Eq. (16) then writes:

$$\frac{T - T_\mathrm{s}}{T - T_\infty} = \frac{1}{\left(\frac{1}{K_\mathrm{kin} \cdot K_\mathrm{heat}} + \frac{\partial P_\mathrm{eq}}{\partial T}(T_\mathrm{s})\right) \cdot K_\mathrm{por} \cdot K_\mathrm{heat}} \tag{18}$$

which quantifies the relative error on the temperature field when the simplified or exact methods are compared. Let us denote by N this dimensionless number which, according to Eq. (6), can be also written:

$$N = \frac{T - T_\mathrm{s}}{T - T_\infty} = \frac{\frac{\mathrm{d}\alpha}{\mathrm{d}t} - \frac{\mathrm{d}\alpha}{\mathrm{d}t}\Big|_\mathrm{s}}{\frac{\mathrm{d}\alpha}{\mathrm{d}t}}. \tag{19}$$

Approximating $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ with $\frac{1}{\tau}$, where τ is the tank loading time, Eq. (19) also becomes:

$$N = \frac{\tau_\mathrm{s} - \tau}{\tau_\mathrm{s}} \tag{20}$$

which represents the relative error on the loading time according to which method is used.

The number N can also be written:

$$N = \frac{1}{\left(\frac{1}{K_\mathrm{kin}} + \frac{\partial P_\mathrm{eq}}{\partial T}(T_\mathrm{s}) \cdot K_\mathrm{heat}\right) \cdot K_\mathrm{por}} \tag{21}$$

where we see that two terms are competing:

- the quantity $\frac{1}{K_\mathrm{kin}}$ stands for the reaction kinetics. When $\frac{1}{K_\mathrm{kin}}$ is large compared to $\frac{\partial P_\mathrm{eq}}{\partial T} \cdot K_\mathrm{heat}$, the reaction kinetic is the slower phenomenon and limits the loading process;
- the quantity $\frac{\partial P_\mathrm{eq}}{\partial T} \cdot K_\mathrm{heat}$ represents the contribution of the heat transfer. If it is large compared to $\frac{1}{K_\mathrm{kin}}$ the diffusion of heat is slow and limits the loading process.

The ratio of those terms allows us to know which one can be neglected. When $\frac{\partial P_{eq}}{\partial T} \cdot K_{heat} \cdot K_{kin} \gg 1$ the system is said as "heat diffusion limited". In this case, using the expression of K_{por} and K_{heat} (Eqs. (6) and (10)) the parameter N becomes:

$$N = \frac{\lambda \cdot M \cdot L_{gas}^2 \cdot \mu}{\frac{\partial P_{eq}}{\partial T}(T_s) \cdot \Delta H \cdot \rho_g \cdot K \cdot L_{heat}^2} \tag{22}$$

When $N \ll 1$, the effect of the flow on the loading process can be neglected without altering significantly the estimation of the duration of the hydrogen loading and of the temperature field. Otherwise, when $N \gg 1$, the flow field equations should be incorporated into the numerical model.

3. Example on classical tank geometries

In this section, the validity of the dimensionless number N will be tested on classical hydride tank geometries which have been reported in various hydride tank studies [2,5,16,8–11] as shown in Fig. 3. Each one of the cases shown in this figure displays a situation corresponding to absorption, i.e., Hydrogen is entering the tank and heat is being released from the bed towards the external walls.

Fig. 3a shows a planar tank where heat is removed from the bottom whereas hydrogen is fed through the top side. Such geometry has been reported in [16] for example and could be of interest in a near future when plate-type heat exchangers geometry will be considered for hydrogen storage. The axisymmetric tank shown in Fig. 3b has a lateral isothermal wall which removes (or brings) the heat of the reaction. The flow field is homogeneously distributed in the radial direction owing to a porous filter which is located along the symmetry axis and which is not shown in Fig. 3b. In both geometries, typical length can be defined for gas diffusion (L_{gas}) and heat diffusion (L_{heat}). Although these two lengths are equal in Fig. 3a and b, they can be different as shown in the more general geometry of Fig. 3c where an axisymmetric tank has a lateral cooled wall and where hydrogen is introduced through the whole section of the top of the bed. In this case, the hydrogen flow has a weak radial velocity. Nevertheless, the axial length is the most pertinent choice for estimating L_{gas}.

3.1. Description of the numerical model

The same granular material has been considered to modelize these three geometries. Co-milled magnesium with transient metals has been chosen to be the hydrogen storing medium. All thermal and chemical properties are taken from experimental investigations on ball-milled magnesium hydride [1,17].

The finite volume technique implemented in the commercial code Fluent® has been used to model these three tanks. Cases 1 and 2 can be studied with a one-dimensional model whereas case 3 needs a 2D axisymmetric model.

The energy equation which is solved is:

$$\rho \cdot C_p \cdot \frac{\partial T}{\partial t} + \rho_g \cdot C_{p_g} \cdot \nabla(T \cdot \vec{V}) = \lambda \cdot \nabla^2 T + \frac{\rho_m \cdot \mathrm{wt} \cdot (1-\varepsilon) \cdot \Delta H^\circ}{M} \cdot \frac{d\alpha}{dt} \tag{23}$$

where the quantity $\rho \cdot C_p$ has already been defined in Eq. (4). For the reaction between magnesium and hydrogen, enthalpy of reaction in real conditions (ΔH) is assumed to be equal to enthalpy in standard conditions (ΔH°). Then ΔH° will be used in the source term.

The source term at the right-hand side of Eq. (23) is proportional to the reaction velocity. For doped magnesium hydride this velocity has been described in [14] and writes:

$$\frac{d\alpha}{dt} = C_a \cdot \frac{(P - P_{eq})}{P_{eq}} \cdot e^{\frac{-E_a}{RT}} \cdot \frac{2}{3} \cdot \frac{(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}} \tag{24}$$

In the model where the flow solution is solved, the momentum and the continuity equations are:

$$\vec{\nabla} P = \frac{\mu}{K} \cdot \vec{V} \tag{25}$$

$$\varepsilon \cdot \frac{\partial \rho_g}{\partial t} + \nabla(\rho_g \cdot \vec{V}) = \rho_m \cdot \mathrm{wt} \cdot (1-\varepsilon) \cdot \frac{d\alpha}{dt} \tag{26}$$

Eq. (26) includes a sink term to take absorption into account. Table 1 presents the values of the physical parameters which are necessary to the computation.

Hydrogen pressure inlet is constant and equal to 0.8 MPa. The constant temperature wall is at 600 K to provide thermal condition for optimal absorption rate. Heat diffusion controls the hydriding process: $\frac{\partial P_{eq}}{\partial T} \cdot K_{heat} \cdot K_{kin} = 300$. This situation has also been previously described as heat-diffusion limited. Convection can be neglected when compared to conduction heat transfer. Estimating the Peclet number $Pe = \frac{V \cdot L_{gas} \cdot \rho_g \cdot C_{p_g}}{\lambda} = 0.03$ with $V = 10^{-4}$ m/s and $C_{p_g} = 14000$ J/kg/K confirms this assumption.

3.2. Critical value of the N criterion

The three geometries shown in Fig. 3 have been computed with magnesium as the absorbing medium. For each geometry, four computations have been done:

- One computation where the flow is not solved, what corresponds to an infinitely small value of the parameter N, or, equivalently, to an infinite value of the porosity factor K. This situation has been termed as "simplified" in the previous sections of this paper.
- Three computations where the flow equation has been solved and the porosity factor K has been gradually varied whereas the other parameters are kept constant. The values of K have been selected to produce values of N equal to 2.2×10^{-1}, 2.2×10^{-2} and 2.2×10^{-3}, respectively.

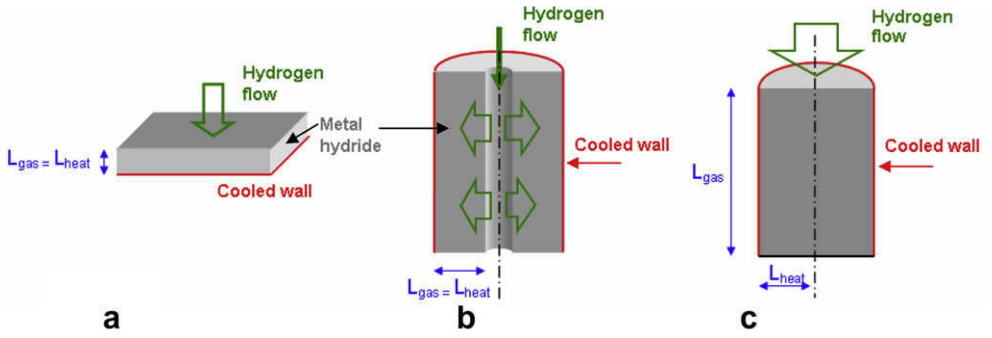

Fig. 3. Planar (a) and cylindrical tank geometry with radial (b) and axial (c) hydrogen diffusion.

Table 1
Physical parameters of the magnesium hydride.

Magnesium hydride	Operating parameters	Hydrogen properties
$C_a = 2.9 \times 10^8\ \mathrm{s}^{-1}$	$T_\infty = 600$ K	$\mu = 8.9\ 10^{-6}$ Pa s
$E_a = 124$ kJ/mol	$P_{in} = 0.8$ MPa	$M = 0.002$ kg/mol
$\Delta H = -75000$ J/mol		
$\Delta S° = -135.6$ J/K mol		
$\rho_m = 1740\ \mathrm{kg/m^3}$		
$\lambda = 0.5$ W/m K		
$\varepsilon = 0.7$		
wt = 0.06 (6 wt% H)		

L_{heat}: case (1) 30 mm; (2) 30 mm; (3) 35 mm.
L_{gas}: case (1) 30 mm; (2) 30 mm; (3) 140 mm.

The time evolution of the volume averaged hydride fraction is reported in Fig. 4.

From Fig. 4, critical values of N can be determined concerning the influence of the flow on the hydriding process. For each case, when N is smaller than 10^{-2}, no difference is visible between the solution where the flow is fully computed and that where the flow is neglected. When N is varied between 10^{-2} and 10^{-1}, the simulations with and without flow are very comparable. When N is greater than 10^{-1} hydriding behavior changes notably: in this case, the effect of the flow is no more negligible.

From these results, it is then remarkable that, whatever the tank geometry, the critical value of N remains the same for each case, i.e., 10^{-1} approximately. Moreover, it is worth reminding that N is representative of the error which is made on the averaged hydriding fraction when the flow field is overlooked.

The expression of the parameter N which has been developed in Section 2 was not depending upon a particular material or a specific geometry. Thus, it is necessary to check that changing the physical properties of the absorbing medium described in Table 1 or changing the values of the length scales L_{heat} and L_{gas} does not affect significantly the critical value of the parameter N. For this purpose, we have only considered the geometry shown in Fig. 3a. The results are presented in Fig. 5a–d. For each case, three computations have been done: one where the flow is neglected, what is equivalent to $N \to 0$) and two others where the flow is taken into account together with values $N = 2.2 \times 10^{-1}$ and $N = 2.2 \times 10^{-2}$ which have been obtained by changing the value of the permeability K. The results can be commented as follows:

- In Fig. 5a, the reaction enthalpy, which is the energy released during the hydriding reaction, has been divided by 10 (while $\frac{\partial P_{eq}}{\partial T}$ has been kept unchanged). The hydriding time is then reduced. With a smaller value of ΔH, we see that the critical value of N still remains around 10^{-1}.
- The effect of changing the length scales L_{heat} and L_{gas} has been tested in Fig. 5b: again, no sensible effect is to be seen on the critical value of N.
- Changing the thermal conductivity of the bed has been tested in Fig. 5c and d where λ has been multiplied by a factor 10 and 100, with respect to the values defined in Table 1. In Fig. 5c, no change in the critical value of N is visible. This confirms that the N criterion is valid for different hydrogen storage materials as long as heat diffusion is the physical phenomenon that controls the hydriding process. On the contrary, when the thermal conductivity is increased by a factor 100, heat diffusion becomes

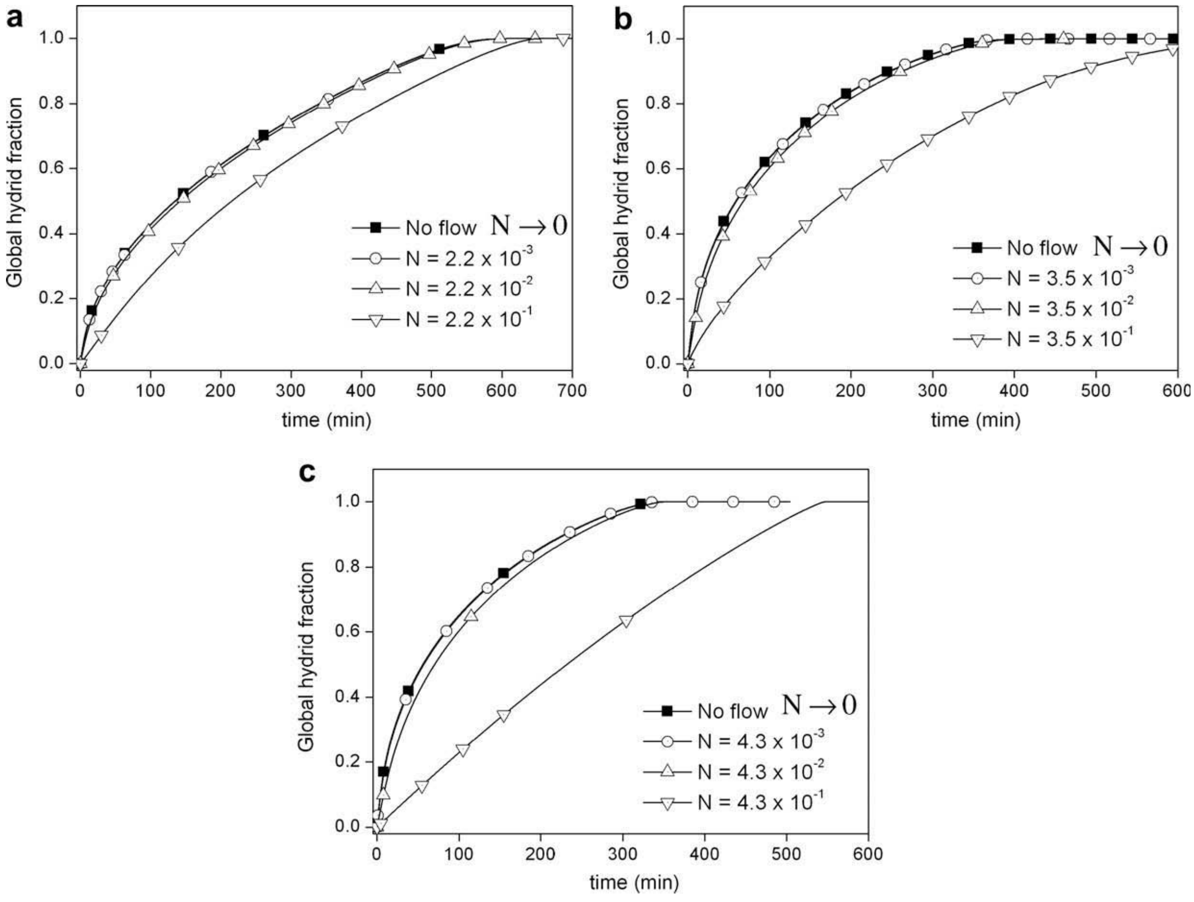

Fig. 4. Hydriding simulations for geometries (a), (b) and (c) with different values of N compared to simulation without flow ($N \to 0$).

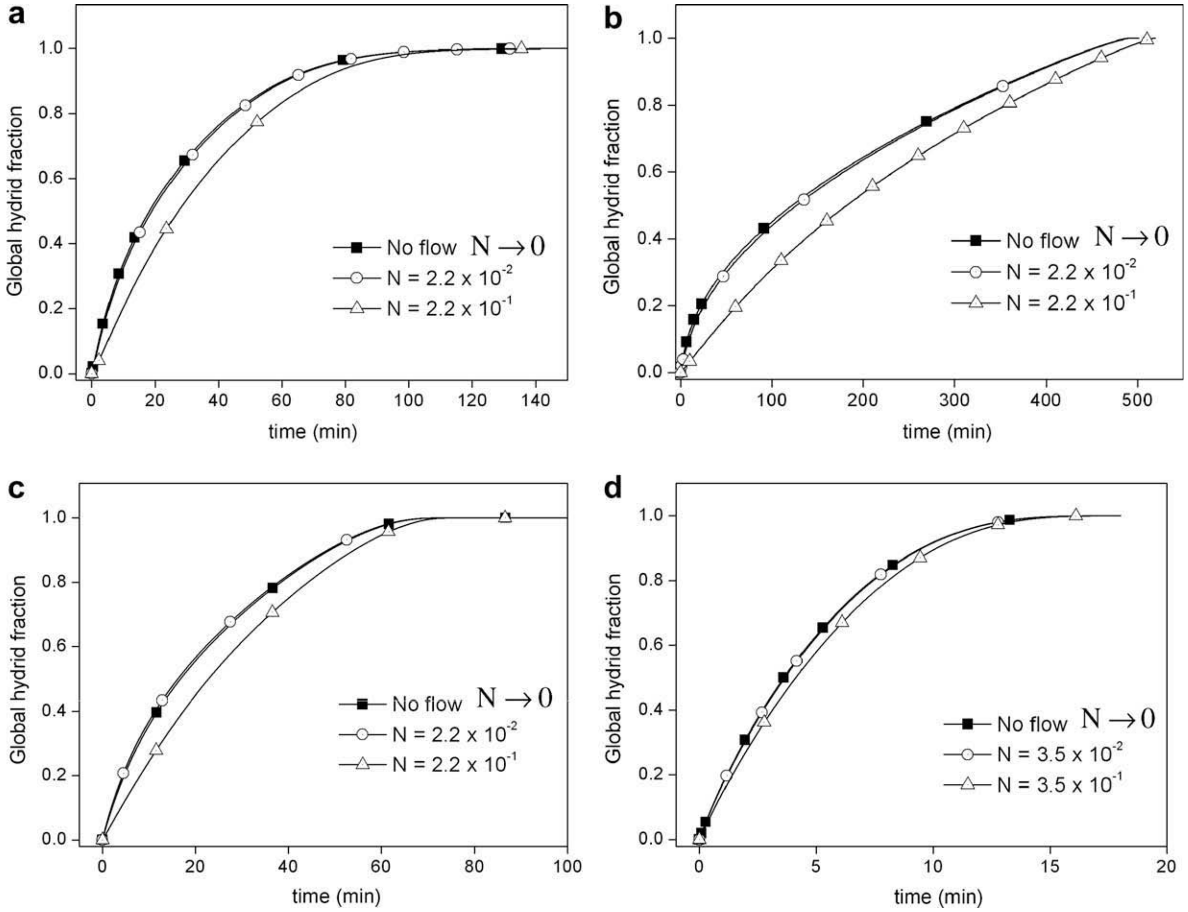

Fig. 5. Hydriding simulations with lower enthalpy (a), extended size of the system (b), and higher thermal conductivity (c and d), with different values of K compared with simulation without flow. The geometry is that of Fig. 3a.

very fast and the ratio $\frac{\partial P_{eq}}{\partial T} \cdot K_{heat} \cdot K_{kin}$ is no more much greater than unity as its value is 3. In this case, heat diffusion does not controls the hydriding process any more and simulations with different values of N show that transition occurs for N superior to 10^{-1}.

4. Considering flow in a real case

An experimental tank and its numerical model are now considered to check the validity of the N parameter. The tank has been designed and tested at the Grenoble NEEL Institute. The cylindrical vessel (Fig. 6) contains 250 g of ball-milled magnesium with transition metal additives. The powder porosity has been reduced by compression so that the material is disk shaped. Since the porosity of the material is low ($\varepsilon = 0.31$), the permeability is relatively poor ($K = 1.7 \times 10^{-15}$ m^2). In order to improve the gas circulation into the tank, it has been necessary to fill it with several of these fine 9 mm-thick compacted disks between which a 1 mm free space has been left for hydrogen radial circulation. For the same reason, their diameter is 1 mm less than the inner tank diameter.

Temperatures are measured in three points ($Tc1$, $Tc2$, $Tc4$) and hydrogen pressure is recorded around the disks. Mass-flow is recorded and integrated to calculate the quantity of hydrogen that has been absorbed.

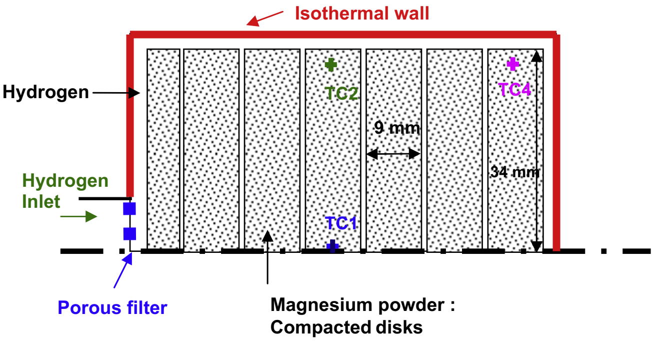

Fig. 6. Sketch of our experimental magnesium cylindrical tank.

Table 2
Parameters used in the modeling of the experimental magnesium tank.

$C_a = 2.9 \times 10^8$ s^{-1}
$E_a = 124000$ J/mol
$\varepsilon = 0.31$
$\Delta H = -75{,}000$ J/mol
$K = 1.7 \times 10^{-15}$ m^2
$L_{gas} = 4.5$ mm
$L_{heat} = 34$ mm
$\lambda = 8$ W/m K
$M = 0.002$ kg/mol
$\mu = 8.9 \times 10^{-6}$ Pa s
$\rho_m = 1740$ kg/m^3
$\rho_g = 0.32$ kg/m^3 (@ 7.7 bar and 600 K)
$\Delta S = -135.6$ J/mol K
wt = 0.06

A complete simulation of the experimental tank has been done, taking the flow field into account. The various parameters of the calculation are presented in Table 2. A wall temperature equal to 297 °C and an inlet pressure of 0.77 MPa have been imposed during the tank loading (Fig. 7). The constant temperature assumption for the walls is due to the great mass of stainless steel and aluminum which is surrounding the powder bed. Since the heat of reaction is absorbed by this shell, its temperature variations remain weak during the loading time. Time evolution of temperatures, pressure around the compacted disks, and absorbed volume of hydrogen are plotted. The pressure in the powder bed is not constant in time during the process owing to the presence of a porous filter at the hydrogen inlet that induces a head loss proportional to the mass-flow rate. Consequently, the gas pressure inside the tank will be lower than the inlet pressure which is imposed by the hydrogen supply network of the laboratory. Because of the exothermic nature of the reaction, temperatures first rise during absorption before to decrease when the bulk of the powder is fully hydrided.

Let us now calculate the value of the above-defined N criterion. First of all we find that the ratio $\frac{\partial P_{eq}}{\partial T} \cdot K_{heat} \cdot K_{kin}$ which allows to check if the reaction is limited by heat diffusion is equal to 15 what is clearly greater than unity. There is no doubt that the reaction is here limited by heat removal rather by the kinetics. The Peclet number is low ($Pe = 3.10^{-2}$) confirming that heat convection is negligible compared to conduction. Finally, the parameter N is found equal to 0.024 and is much smaller that unity.

Still for the same experimental tank, Fig. 8 reports simulations made with and without the flow computation. When the flow is not computed, the value of the pressure is calculated in a simple external program which makes a balance of the gas inflow and of its inner consumption inside the tank.

Fig. 8 shows that there is almost no difference between the two kinds of simulations. The low value of N together with the weak difference between the runs made with or without the flow confirms that the effect of the flow is really negligible in the case under study. The parameter N is clearly an indicator which tells whether or not the flow computation can be ignored.

Fig. 9 shows several simulations where the value of N has been varied between 2×10^{-1} and 2×10^{-4} by changing the value of the permeability K. A small value of N produces no difference between the calculation made with or without the flow computation. Increasing the value of N up to 0.2 shows the appearance of a small discrepancy.

It is then possible to conclude that as long as the parameter N remains smaller than, say, 0.1, the fluid mechanics problem has not to be solved.

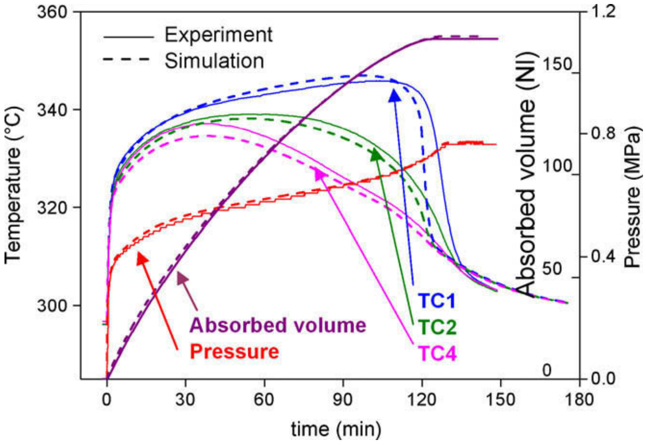

Fig. 7. Computed and experimental evolution of temperature, pressure and volume absorbed during the hydrogen loading of the magnesium tank.

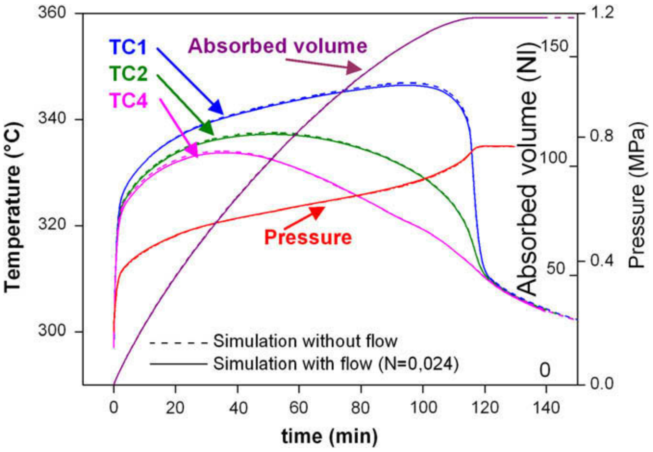

Fig. 8. Simulation of the loading of a MgH_2 reactor with and without solving the flow.

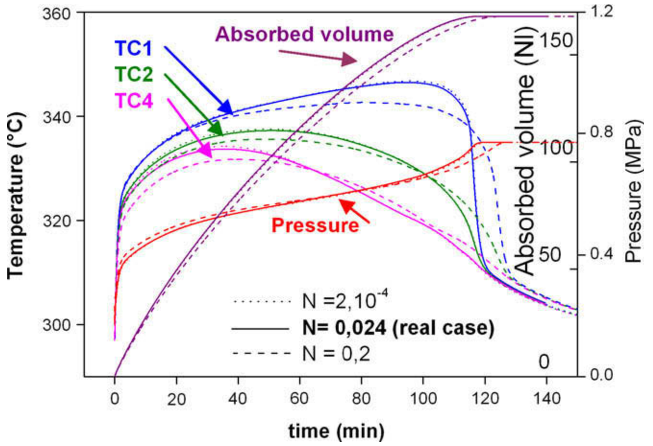

Fig. 9. Influence of the parameter N on the simulated tank loading.

As seen in Fig. 9, higher values of N increase the loading time as a loss of pressure inside the compacted disks slows down the kinetics. From a practical point of view, the N parameter should be used to determine the optimal dimensions of the compacted disks (L_{gas} and L_{heat}) in order to optimize the loading time.

5. Conclusion

Using simple equations that link hydriding velocity to heat and mass transfer in the porous absorbing bed, a dimensionless criterion N has been found to estimate the relative error committed on the hydriding time when the resolution of the flow equation is omitted:

$$N = \frac{\lambda \cdot M \cdot L_{gas}^2 \cdot \mu}{P_{eq} \cdot \frac{\Delta H^2}{RT^2} \cdot \rho_g \cdot K \cdot L_{heat}^2}$$

It has been found that as long as N remains lower than 0.1 approximately, the fluid flow can be ignored in the simulation of the tank. The criterion N can be used only when conductive heat transfers limit the hydriding reaction in the tank and is large beside convective and radiation heat transfer. This criterion has been successfully tested on a magnesium experimental tank. It can be successfully applied to any geometry provided that a careful analysis of the heat and mass transfer has been previously done in order to introduce pertinent values of the length scales L_{heat} and L_{gas}.

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