Feasibility analysis of a novel solid-state H$_2$ storage reactor concept based on thermochemical heat storage: MgH$_2$ and Mg(OH)$_2$ as reference materials

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Abstract

This paper discusses the feasibility of a novel adiabatic magnesium hydride (MgH$_2$) reactor concept based on thermochemical heat storage. In such a concept, the heat of reaction released during the absorption of hydrogen is stored by a thermochemical material in order to be reused in a subsequent desorption stage. Magnesium hydroxide (Mg(OH)$_2$) has been selected as the suitable material for integration into the MgH$_2$ storage system due to its thermodynamic properties. An analytical formulation of hydrogen absorption time is used to determine the range of the geometrical characteristics of the two storage media, their properties and their operating conditions. The advantage of the proposed new concept is the possibility to reduce the mass of the heat storage media by a factor of 4 compared to phase change material, improving then the gravimetric system capacity as well as its total cost. The second advantage is an improved flexibility of the operating pressure conditions for MgH$_2$ absorption reaction and Mg(OH)$_2$ dehydration reaction that enables shorter hydrogen absorption times by ensuring larger temperature gradients between the two storage media.

Keywords

Hydrogen storage
Thermochemical heat storage
Magnesium hydride
Magnesium hydroxide
Hydrogen absorption time
Analytical study

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1. Introduction

After decades of intensive research on metal hydrides, today, there is a tremendous volume of data covering their properties and application areas [1–5]. One of the traditional applications of these materials is the storage of hydrogen for fuel cell operation as they offer compact systems at rather low pressures. However, due to their high weight, current applications focus on heavy-duty vehicles or stationary devices.

One material that has been proposed in several publications for stationary hydrogen storage is magnesium hydride (MgH_2). This material is cheap and offers still high gravimetric capacities of up to 7.6 wt.% [6]. However, the main drawback of this material is the low system efficiency, as it can only be operated at temperatures in the range of 300 to 400 °C due to thermodynamic and kinetic limitations. Thus, in contrast to most metal hydride systems where the focus is on a reactor design with improved heat transfer [7], for magnesium hydride, heat integration is the main challenge.

Furthermore, the MgH_2 enthalpy of reaction corresponds to up to 31% of the lower heating value of the absorbed hydrogen [8]. Thus, solutions have to be found to avoid a decrease of the system efficiency. One option is through systems where the magnesium hydride storage tank is coupled with a high temperature solid oxide fuel cell (SOFC) using a diathermic heat transfer fluid that has to be pumped [9]. Thus, the heat is provided using the waste heat of the fuel cell by a *system integration*.

In order to simplify the system complexity, previously, a magnesium hydride reactor concept has been proposed by Garrier et al. [8] that *stores* the reaction enthalpy during absorption for the subsequent desorption process in a phase-change material (PCM). The selection criteria were based on a stable PCM with high melting enthalpy, high thermal conductivity, and a melting temperature in between the equilibrium temperatures of absorption and desorption, so that the heat of reaction is conducted from one media to another due to the presence of temperature gradient. An optimization study has shown that the eutectic $Mg_{69}Zn_{28}Al_3$ is a suitable PCM to be integrated into the MgH_2 storage system and a large-scale magnesium hydride tank with a total hydrogen storage capacity of 7050 Nl has been successfully built and tested with main use for stationary applications.

In this paper, an alternative to such a PCM is presented that stores the heat released during the hydrogen uptake in a *thermochemical material* for the subsequent desorption. Similarly to the storage of hydrogen, the thermochemical heat storage involves reversible chemical reactions between solid and gas, mostly water vapor. The synthesis of the solid is exothermic, while its decomposition requires heat input [10]. In comparison to the sensible and latent heat storage methods, *thermochemical energy storage technologies* offer higher energy densities and longer-term preservation ability for thermal energy [11]. They have gained a lot of interest for heat pumping, heat storage, e.g. solar energy and waste heat recovery in industrial processes [12–16].

In case of hydrogen storage based applications and to the best of our knowledge, there has been no research performed so far to investigate the hydrogen loading process in an adiabatic hydrogen storage system based on the combination of a metal hydride and a thermochemical heat storage material. The proposed reactor design consists of an adiabatic system where heat is exchanged internally/reversibly between magnesium hydride and a suitable thermochemical material. Thus, the aim of this paper is (i) to discuss the feasibility of such a new reactor concept through the identification of the

suitable thermochemical storage material to be combined with magnesium hydride, (ii) to present an analytical formulation of the hydrogen loading time, which would be used as preliminary calculation tool to identify the range of parameters for the two combined media in order to optimize the hydrogen loading process, and finally (iii) to discuss the competitiveness of this concept compared to the existing technology.

2. Basic Concept

For such a new hydrogen storage system based on the combination of magnesium hydride and a thermochemical material, the heat of reaction released by the metal hydride during the absorption of hydrogen will be stored by the thermochemical material, and it will be given back during the desorption stage (similar to the system with PCM). The choice of the heat storage material to be combined with the MgH_2 is based on the two materials reaction temperatures, their energy storage densities and their reaction rates. In addition, the two materials should have good reaction reversibility and durability, and good mass and heat transfer properties. No toxicity, corrosion resistance, availability and low cost are also among the criteria to be considered when selecting the material to be combined with the magnesium hydride.

2.1. Identification of the suitable thermochemical material

Hydrogen storage media

As outlined in the introduction, magnesium hydride has been proposed as a suitable candidate for hydrogen-based stationary applications owing to its high gravimetric capacity of 7.6 wt.%, low cost, and light weight. In addition, considerable improvements of its kinetics and thermal properties have been achieved in the past, so that today it is commercially available in form of pellets with stable sorption properties and efficient thermal conductivity [17]. Moreover, the same material has been selected for the development of hydrogen storage system using phase-change material to store the heat of reaction [8]. Thus, by referring to the related study, it is possible to compare the performance of the magnesium hydride reactor based on latent heat storage and the one using thermochemical heat storage in order to conclude about the relevance of the new reactor concept investigated in this study.

Magnesium hydride absorbs and desorbs hydrogen following the reversible reaction

$$Mg(s) + H_2(g) \Leftrightarrow MgH_2(s) + 75 \text{ kJ mol}^{-1}{}_{H_2} \qquad (1)$$
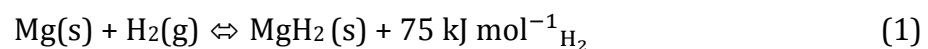
The hydrogen uptake is an exothermic process and the heat of reaction should be removed, otherwise the temperature of MgH_2 media reaches the corresponding equilibrium temperature and the absorption of hydrogen is either slowed down or stopped. During the endothermic reaction of hydrogen release, heat supply is required.

Thermochemical heat storage media

For thermochemical systems, the thermal energy can be reversibly stored and released based on the following chemical reaction [10]:

$$A + B \Leftrightarrow C + Heat \qquad (2)$$

During the forward reaction, A and B are combined together to form the product C while releasing heat. In principle various gas-solid reactions are possible, e.g. reactions with water vapor, CO_2, ammonia or hydrogen. With heat supply, the thermochemical material C is dissociated into components A and B.

Salt hydrates, ammonia, hydroxides, carbonates and metals can potentially be used for thermochemical storage applications. Kuravi et al. [14] presented a list of these most promising candidates with the range of their operating temperatures and reaction enthalpies. As first attempt to determine the thermochemical material suitable for integration into MgH_2 storage system, our focus has been directed to identifying one of those heat storage media with the same range of reaction temperature as magnesium hydride (*250 °C - 400 °C*) [18]. Such a selection criteria has restricted our choice to magnesium hydroxide, $Mg(OH)_2$ as possible candidate to be combined with magnesium hydride.

The decomposition/synthesis of the $Mg(OH)_2$ system is based on the following reversible chemical reaction

$$Mg(OH)_2\,(s) + 81\ kJ\ mol^{-1}{}_{Mg(OH)_2} \Leftrightarrow MgO(s) + H_2O(g) \qquad (3)$$
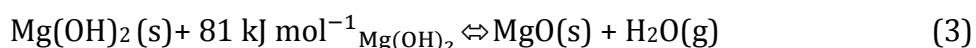
The charging process corresponds to the forward endothermic dehydration reaction where heat is stored and magnesium hydroxide is dissociated to magnesium oxide and water vapor. The reverse exothermic hydration reaction constitutes the thermal discharging process where heat is released and magnesium oxide reacts with water vapor to form magnesium hydroxide.

The "$MgO/H_2O/Mg(OH)_2$" system has mainly been investigated by Kato et al. [19–23] for medium temperature chemical heat pump applications. Their research has focused first on the development of a new magnesium oxide material using ultra fine oxide powder as precursor in order to improve its durability [20]. Subsequently, the same developed material has been used to test the performance of different packed bed reactor configurations of $MgO/Mg(OH)_2$ chemical heat pumps [22,23], to study the reaction mechanism of the material mixed with different additives such as LiCl [24], LiBr [25–27] and $CaCl_2$ [28,29], and to improve its thermal properties by addition of expanded graphite [30–32]. The related results have shown the potential of the studied material to meet the requirements of the chemical heat storage/chemical heat pump technology.

In the current study, the same thermodynamic and thermal properties of the $Mg(OH)_2$ investigated by Kato and coworkers are used (i) to discuss the feasibility of a MgH_2 reactor using $Mg(OH)_2$ as thermochemical material to store the heat of reaction and (ii) to describe in detail the operational principle of this new reactor concept.

To avoid any confusion between the description of hydrogen and thermochemical systems, in the following text the designations of *absorption* and *desorption* reactions are used to describe *hydrogen uptake* and *release* for MgH_2 system, respectively; whereas the designations of *hydration* and *dehydration* reactions are used to describe *discharging* and *charging* processes for $MgO/Mg(OH)_2$ system, respectively.

2.2. Thermodynamic considerations

The feasibility of the new MgH_2 reactor concept investigated in this study depends on the thermodynamic properties of used hydrogen and thermochemical heat storage materials. Based on the studies elaborated by Chaise et al. [18] and Kato et al. [19], the equilibrium diagrams of the two studied systems are shown in Fig. 1 within the range of their operating temperatures and pressures.

For Mg/MgH_2 system, the selection of the applied pressures during hydrogen uptake and release determines the equilibrium absorption and desorption temperatures to be reached by the hydrogen storage media. Based on the experience gained in practical

operational conditions of MgH_2 tanks, the absorption and desorption pressures, P_{abs} and P_{des} are set at 1 MPa and 0.2 MPa, respectively. This corresponds to equilibrium absorption and desorption temperatures, $T_{eq,abs}$ and $T_{eq,des}$, of 370 and 305 °C as can be seen from Fig. 1.
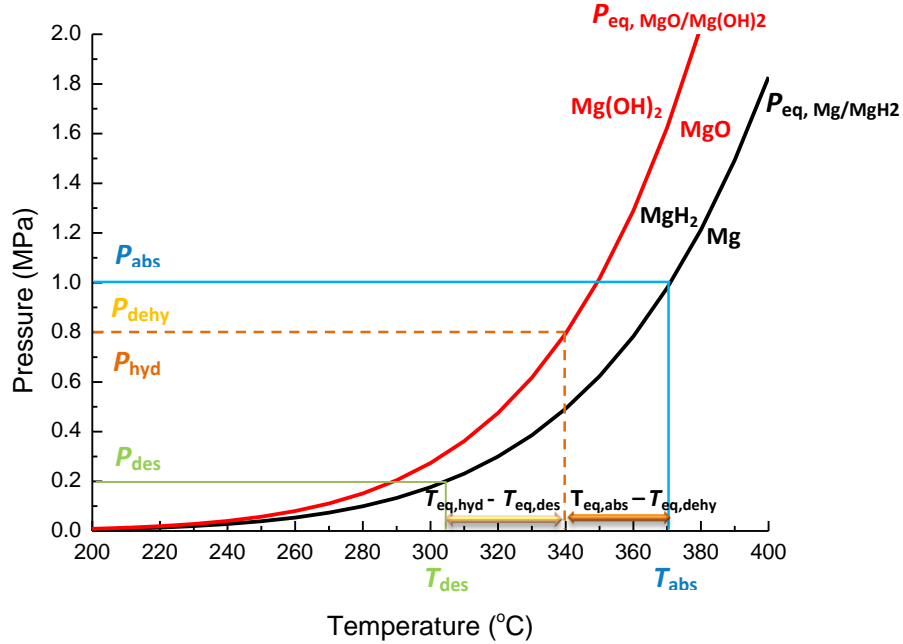

Fig. 1. Pressure-Temperature phase diagrams for Mg/MgH_2 and $MgO/Mg(OH)_2$ systems.

As described earlier, the heat of reaction released by MgH_2 during its exothermic absorption reaction should be consumed during the endothermic dehydration of $Mg(OH)_2$. To ensure the transfer of heat between the two media, a temperature gradient between Mg/MgH_2 and $MgO/Mg(OH)_2$ systems is required. Specifically, the dehydration of $Mg(OH)_2$ should occur at a temperature, $T_{eq,dehy}$, lower than the absorption temperature of the magnesium hydride at 1 MPa ($T_{eq,dehy} < T_{eq,abs} = 370$ °C). As first step to assess the feasibility of this new reactor concept, $T_{eq,dehy}$ is set to 340 °C, corresponding to the melting temperature of the PCM used in [8]. Referring to the equilibrium diagram of $MgO/Mg(OH)_2$ system plotted in Fig. 1, this is equivalent to $Mg(OH)_2$ dehydration pressure, $P_{dehy,eq}$ of 0.8 MPa. This means that in order to drive the thermochemical system towards the dissociation reaction of $Mg(OH)_2$ at this temperature level, the pressure P_{dehy} should be lower than 0.8 MPa.

Indeed, referring to Kato and coworkers studies [26,28], the $Mg/Mg(OH)_2$ system can store heat at around 300 °C (lower than the PCM melting temperature) under *vacuum* while achieving reasonable dehydration reaction rates.

In analogy, to transfer the heat released during the exothermic hydration of MgO towards MgH_2 media desorbing hydrogen, the hydration temperature, $T_{eq,hyd}$ should be higher than the desorption temperature, $T_{eq,des}$ to be reached at 0.2 MPa ($T_{hyd} > T_{des} = 305$ °C). Again, by setting $T_{eq,hyd} = 340$ °C, this means that a hydration pressure, P_{hyd} higher than 0.8 MPa is required to drive the thermochemical system towards the hydration reaction of MgO at this temperature level.

So far, the hydration reaction has only been investigated up to a pressure of 0.4 MPa [23]. However, since reported reaction rates are sufficiently high, the $Mg/Mg(OH)_2$ system is an appropriate reference system for the purpose of this study.

2.3. Operating principle

The operating principle of the adiabatic MgH_2 reactor based on thermochemical heat storage is shown in Fig. 2. The proposed new system consists of a reactor combining both, (Mg/MgH_2) and $(Mg(OH)_2/MgO)$ systems separated by a wall, and a water reservoir. It has two operation modes: "Absorption of H_2/Dehydration/Condensation of $H_2O_{(g)}$" and "Desorption of H_2/Hydration/Evaporation of $H_2O_{(l)}$".

In "Absorption of H_2/Dehydration/Condensation of $H_2O_{(g)}$" mode (Fig. 2(a)), the absorption and dehydration reactions of the two storage media occur simultaneously at two different temperature levels: hydrogen is absorbed at $T_{eq,abs}$ and magnesium hydroxide is dehydrated by consuming the hydride reaction heat, Q_{abs} at lower temperature, $T_{eq,deh}$. The generated water vapor is condensed at the water reservoir at T_c while releasing condensation heat, Q_c.

In "Desorption of H_2/Hydration/Evaporation of $H_2O_{(l)}$" mode (Fig. 2(b)), the system consists initially of magnesium hydride and magnesium oxide. The condensed water in the reservoir is heated up by consuming evaporation heat, Q_v of 40 kJ/mol H_2O. The produced vapor at T_v reacts with magnesium oxide and the thermochemical heat storage media reaches temperature, $T_{eq,hyd}$, while releasing the hydration heat, Q_{hyd}. Due to the temperature gradient between the thermochemical heat storage media and hydrogen storage media, the hydration reaction heat is conducted towards magnesium hydride bed and the desorption of hydrogen occurs at temperature, $T_{eq,des}$, lower than the one reached by the MgO bed ($T_{eq,hyd}$).
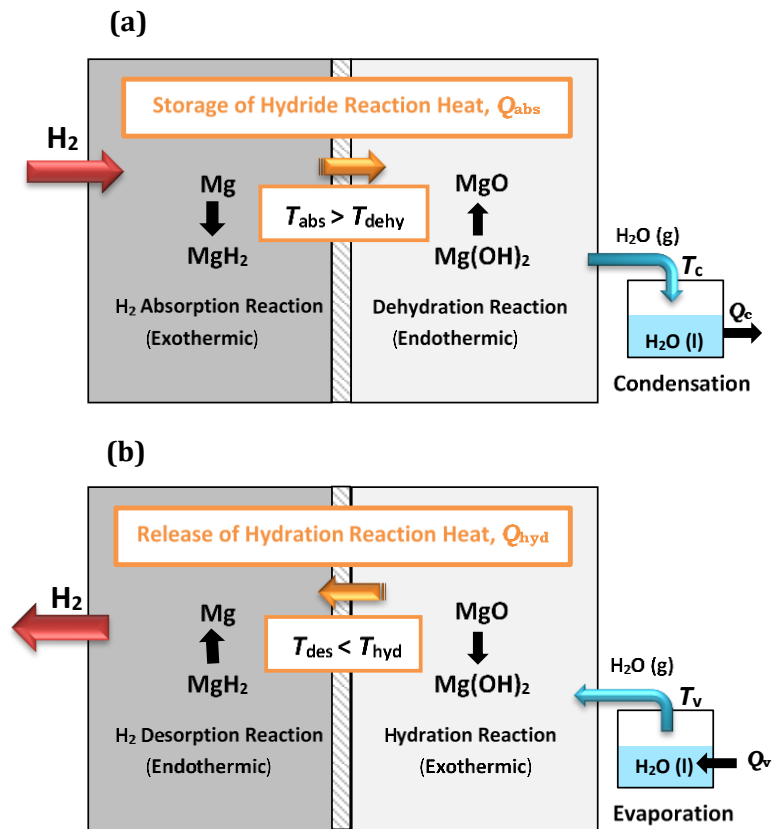

Fig. 2. Operating principle of magnesium hydride reactor using magnesium hydroxide as heat storage media: (a) Absorption of H_2 /Dehydration of $Mg(OH)_2$/Condensation of H_2O and (b) Desorption of H_2 /Hydration of MgO/Evaporation of H_2O.

In our reference case, the required heat to evaporate water has to be provided at T_v of 170 °C to 180 °C due to the heat pump effect of the thermochemical storage [23]. Indeed, for this temperature range, the corresponding water vapor pressure is between 0.824 MPa and 1.05 MPa. This will result in an equilibrium hydration temperature, $T_{eq,hyd}$ greater than or equal to 340 °C (see the van't Hoff diagram in Fig. 1) which is much higher than 305 °C, the equilibrium desorption temperature of the MgH_2 bed desorbing hydrogen at 0.2 MPa (see discussion in the previous subsection). For the required T_v in this system, the temperature level of the exhaust heat of a High temperature (HT) polymer electrolyte membrane fuel cells (PEMFCs) is sufficient in contrast to systems with direct heat integration based on SOFCs. Furthermore, depending on the choice of reaction system, it is also possible to directly integrate the water vapor leaving the HT-PEMFC into the thermochemical storage.

3. Analytical formulation

After the selection of the suitable thermochemical material to be combined with the magnesium hydride, a first estimate of the charging performance is presented in this section. As for stationary applications, a hydrogen loading time of 5 hours is acceptable [8], it is assessed if the new MgH_2 reactor concept investigated in this study, could be filled with hydrogen in a time interval of 5 hours or less. This is closely related to the efficient thermal management of the reaction heat released during the hydrogen uptake: this heat should be quickly conducted to the thermochemical heat storage media to ensure that the temperature of the MgH_2 bed does not reach the equilibrium, resulting then in the slowdown of the hydrogen storage process. The efficient heat transfer between the hydrogen and heat storage media depends on these materials properties as well as the reactor design parameters.

Before performing numerical and experimental studies to investigate the hydrogen loading process in this MgH_2 reactor based on thermochemical heat storage, the development of an analytical expression of hydrogen absorption time is a good approach for evaluating the performance of the selected materials and directing research efforts for possible improvement of their properties. At the same time, it serves as preliminary calculation tool to optimize hydride and thermochemical materials thicknesses recognized as key design parameters [33–35].

Marty et al. [35] developed analytical expressions of loading times for various geometries of MgH_2 reactor based on latent heat storage and a good agreement was obtained by comparing the calculated values to numerical and experimental results. Here, the same calculation approach is adapted to the MgH_2 system based on thermochemical heat storage in order to evaluate its related hydrogen absorption time. The investigated reactor can be represented as a series of rectangular cells or cylindrical tubes where MgH_2 and $Mg(OH)_2$ beds are combined and a separation layer is used to ensure the indirect contact between the two media. Figure 3(a), (b) illustrates a single cell of one rectangular and cylindrical MgH_2 and $Mg(OH)_2$ shaped bed.

In order to describe such an adiabatic hydrogen storage reactor based on a thermochemical system, a new analytical equation has been formulated based on the following assumptions:

- The heat transfer process in H_2 storage media and heat storage media is one dimensional and due only to conduction.

- The H_2 absorption reaction and the $Mg(OH)_2$ dehydration reaction are controlled only by heat transfer (the kinetics is not the limiting step for the two systems, Mg/MgH_2 and $MgO/Mg(OH)_2$).
- The hydrogen absorption front and the $Mg(OH)_2$ dehydration front are moving into opposite directions.
- The heat released during the absorption of hydrogen in the magnesium hydride domain at the time interval, dt and in the elementary volume, dv_{MgH_2} is used to dehydrate the magnesium hydroxide at the same time interval in the elementary volume, $dv_{Mg(OH)_2}$.
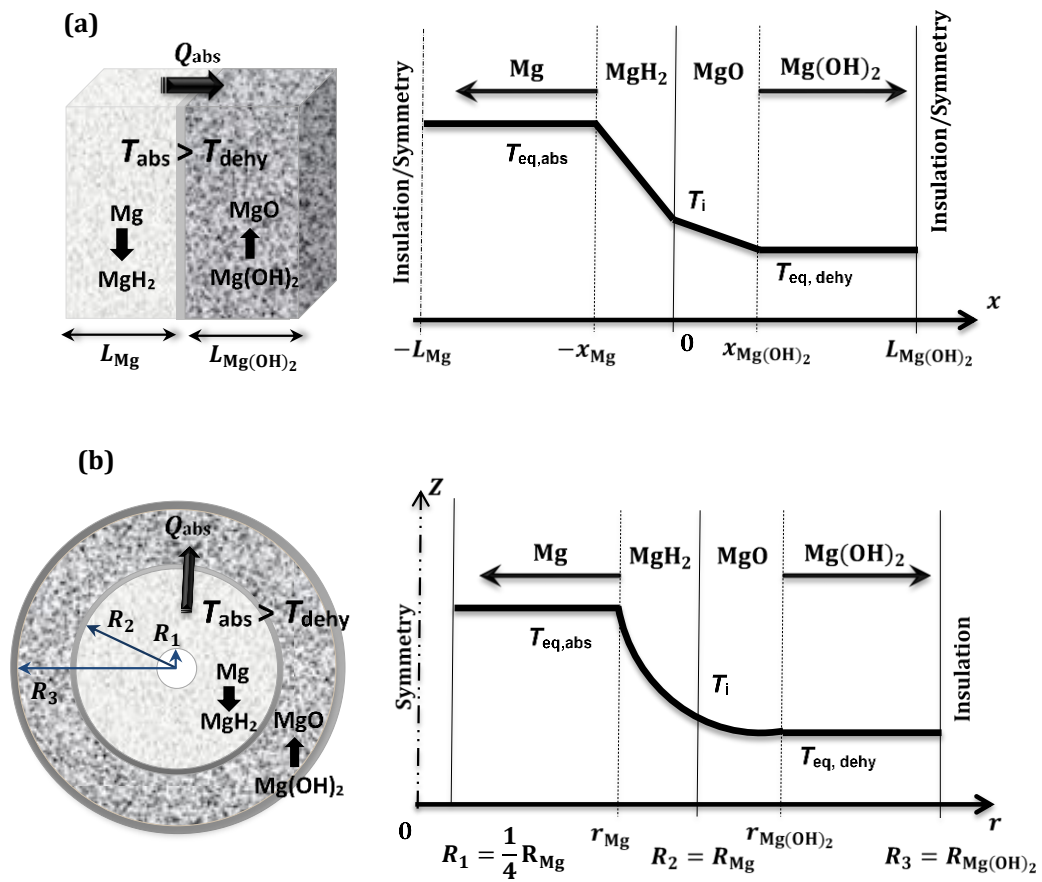- A perfect thermal contact between H_2 storage media and heat storage media is assumed.

Fig. 3. Schematic of the used geometry in the analytical study showing the hydrogen absorption front and the $Mg(OH)_2$ dehydration front in (a) rectangular and (b) cylindrical coordinates.

3.1. Rectangular geometry of Mg/MgH_2 and $MgO/Mg(OH)_2$ beds

Figure 3(a) shows a schematic drawing of the computational domains of Mg/MgH_2 and $MgO/Mg(OH)_2$ beds in case of one rectangular single cell where symmetry or insulation boundary conditions can be applied on both media sides.

The H_2 absorption front and the $Mg(OH)_2$ dehydration front are moving into opposite directions. Due to the presence of a temperature gradient between the two media, the heat of reaction released during the absorption of hydrogen, Q_{abs} is conducted towards the magnesium hydroxide media and it is stored during the $Mg(OH)_2$ dehydration reaction. Hence, magnesium hydride media and magnesium hydroxide media are respectively, cooled and heated faster in the contact zones characterized by lengths x_{Mg}

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and $x_{\mathrm{Mg(OH)_2}}$ as shown in Fig. 3(a). As a result, these two zones saturate earlier than the rest of magnesium hydride and magnesium hydroxide beds where the respective equilibrium temperatures, $T_{\mathrm{eq,abs}}$ and $T_{\mathrm{eq,dehy}}$ are reached. Once the storage of absorption heat, Q_{abs} is completed, the hydrogen storage media and heat storage media are characterized by their thicknesses, L_{Mg} and $L_{\mathrm{Mg(OH)_2}}$ and the hydrogen absorption time can be expressed as [35]

$$t_{\mathrm{abs}} = L_{\mathrm{Mg}}{}^2/(2A)\cdot(1+\lambda/K) \tag{4}$$

where $A = \lambda_{\mathrm{Mg}}\cdot M_{\mathrm{H_2}}\left(T_{\mathrm{eq,abs}} - T_{\mathrm{eq,dehy}}\right)/\left((1-\varepsilon)\rho_{\mathrm{Mg}}w_t\Delta H_{\mathrm{Mg}}\right)$ is the ratio of the sensible heat transferred between the MgH$_2$ and Mg(OH)$_2$ beds and the reaction heat released during the absorption of hydrogen and $\lambda = \lambda_{\mathrm{Mg}}/\lambda_{\mathrm{Mg(OH)_2}}$ is the ratio of the thermal conductivities of the two storage media, MgH$_2$ and Mg(OH)$_2$. $K = \Delta x_{\mathrm{deh}}r_{\mathrm{mix}}\rho_{\mathrm{Mg(OH)_2}}\Delta H_{\mathrm{Mg(OH)_2}} \times M_{\mathrm{H_2}}/\left((1-\varepsilon)w_t\rho_{\mathrm{Mg}}\Delta H_{\mathrm{Mg}} \times M_{\mathrm{Mg(OH)_2}}\right)$ is the ratio of the heat stored by the thermochemical material and the heat released during the absorption of hydrogen. It is also equal to the ratio of the two bed thicknesses when the storage of the reaction heat is completed ($K = L_{\mathrm{Mg}}/L_{\mathrm{Mg(OH)_2}}$).

In these expressions, $T_{\mathrm{eq,abs}}$, λ_{Mg}, ε, ρ_{Mg}, w_t and ΔH_{Mg} are the equilibrium absorption temperature, the thermal conductivity, the porosity, the density, the gravimetric capacity and the reaction enthalpy of magnesium hydride, respectively. $T_{\mathrm{eq,dehy}}$, $\lambda_{\mathrm{Mg(OH)_2}}$, $\rho_{\mathrm{Mg(OH)_2}}$ and $\Delta H_{\mathrm{Mg(OH)_2}}$ are the equilibrium dehydration temperature, the thermal conductivity, the density and the reaction enthalpy of magnesium hydroxide, respectively. The dehydrated fraction of water vapor is denoted as Δx_{deh}. In case where Mg(OH)$_2$ is mixed with expanded graphite (EG) to improve its thermal conductivity, the mixing mass ratio, r_{mix} is defined as $m_{\mathrm{Mg(OH)_2}}/(m_{\mathrm{Mg(OH)_2}} + m_{\mathrm{EG}})$ [28].

3.2. Cylindrical geometry of Mg/MgH$_2$ and MgO/Mg(OH)$_2$ beds

In cylindrical geometry, magnesium hydride is introduced in the annular region between R_1 and R_2 and surrounded by magnesium hydroxide in the region between R_2 and R_3, as illustrated in Fig. 3(b). The external surface of the cylindrical tube is adiabatic. Using the same assumptions and heat transfer description given above, the hydrogen absorption time is [35]

$$t_{abs} = R_2^2/(4A)\left\{\chi(ln\chi - 1) + \lambda(1 + K - \chi)[ln((1 + K - \chi)/K) - 1] + 1 + \lambda K\right\} \tag{5}$$

χ is defined as $(R_1/R_2)^2$. The expressions of A, λ and K are the same defined in case of rectangular geometry; however for the expression of K, the complete storage of the reaction heat, Q_{abs} imposes the following relationship between MgH$_2$ and Mg(OH)$_2$ volume: $K = (R_2^2 - R_1^2)/(R_3^2 - R_2^2)$ [35].

4. Results of the analytical formulation

In order to evaluate the hydrogen storage performance of the new MgH$_2$ reactor based on thermochemical heat storage, the hydrogen absorption time is calculated for different MgH$_2$ and Mg(OH)$_2$ beds geometries and thicknesses, different Mg(OH)$_2$ properties and under different operational conditions of pressure and temperature for both materials. The properties of MgH$_2$ and Mg(OH)$_2$ used for calculations are listed in Tables 1 and 2. For magnesium hydride, calculations are performed based on the properties of pelletized material mixed with 5% of expanded natural graphite [36]. For magnesium hydroxide, three options are considered including composite materials made of Mg(OH)$_2$ and expanded graphite (EG) with an optimized mixing ratio, r_{mix} of

8/9, called EM8 and compressed either into (1) pellet shape [31], (2) as a block to match the dimensions of the container [32], or (3) as loose powder of pure $Mg(OH)_2$ filled into an aluminum matrix foam.

4.1. Dependence of the H_2 absorption time on MgH_2 and $Mg(OH)_2$ beds thicknesses

The relationship between the hydrogen absorption time and the MgH_2 and $Mg(OH)_2$ bed thicknesses given by equations 4 and 5 are used to determine the range of geometrical characteristics of hydrogen storage media and heat storage media so that an absorption time of 5 hours, comparable to the one reached in the case of MgH_2 based on latent heat storage, could be achieved [8]. For these calculations, the temperatures of MgH_2 and $Mg(OH)_2$ media are set equal to the equilibrium temperature of MgH_2 at 1 MPa and the melting temperature of $Mg_{69}Zn_{28}Al_3$, 370 °C and 340 °C, respectively. The properties of $Mg(OH)_2$ as EM8 pellets are used (see Table 2) and the dehydrated fraction of water vapor, Δx_{deh} is varied from 50% to 100%, since different values can be achieved depending on the operational conditions of $MgO/Mg(OH)_2$ system as well as its dehydration reaction time [26].

4.1.1. Case of rectangular geometry of Mg/MgH_2 and $MgO/Mg(OH)_2$ beds - Magnesium hydroxide as EM8 pellets

Figure 4(a), (b) shows the evolution of the hydrogen absorption time, t_{abs} and the thickness of $Mg(OH)_2$ media, $L_{Mg(OH)_2}$ as function of the dehydrated fraction of water vapor, Δx_{deh} ranging from 50% to 100% for three selected thicknesses of magnesium hydride bed, L_{Mg} = 0.5 cm, 0.75 cm and 1 cm. For a given value of Δx_{deh}, the increase of MgH_2 bed thickness is accompanied by a significant increase of $Mg(OH)_2$ bed thickness and H_2 absorption time. This is due to the fact that more reaction heat, Q_{abs} is released when thicker MgH_2 media is used. As a result, more $Mg(OH)_2$ material is required to store this reaction heat, and due to its low thermal conductivity of 0.55 W/(m.K), the conduction of Q_{abs} towards the magnesium hydroxide bed is very slow, inhibiting then the fast absorption of hydrogen.

It should also be noted that for a same thickness of MgH_2 bed, higher dehydrated fractions of water vapor, Δx_{deh} result in shorter hydrogen absorption times and thinner $Mg(OH)_2$ thicknesses. Indeed, due to the endothermic nature of $Mg(OH)_2$ dehydration reaction, more heat is required to reach higher dehydrated fractions of water vapor. Therefore, when Δx_{deh} increases and for the same amount of reaction heat, Q_{abs} released by magnesium hydride, less $Mg(OH)_2$ material is needed. As a result, a faster extraction of this reaction heat from MgH_2 media is obtained, which explains the profiles of t_{abs} and $L_{Mg(OH)_2}$ when Δx_{deh} increases.

By recalling that the hydrogen absorption time should be competitive with the one achieved in case of MgH_2 reactor based on latent heat storage, t_{abs} should not exceed in any case 5 hours [8]. For instance, by selecting L_{Mg} = 0.75 cm as reference case, this suggests that a *minimum* dehydrated fraction, Δx_{deh} of 65% is required to reach such a goal (see the green dashed line in Fig. 4(a)), and the resulting $Mg(OH)_2$ bed thickness is equal to 3.25 cm as shown in Fig. 4(b) (green dotted line). Shorter hydrogen absorption times can be expected for higher Δx_{deh} and thinner $Mg(OH)_2$ bed thicknesses.
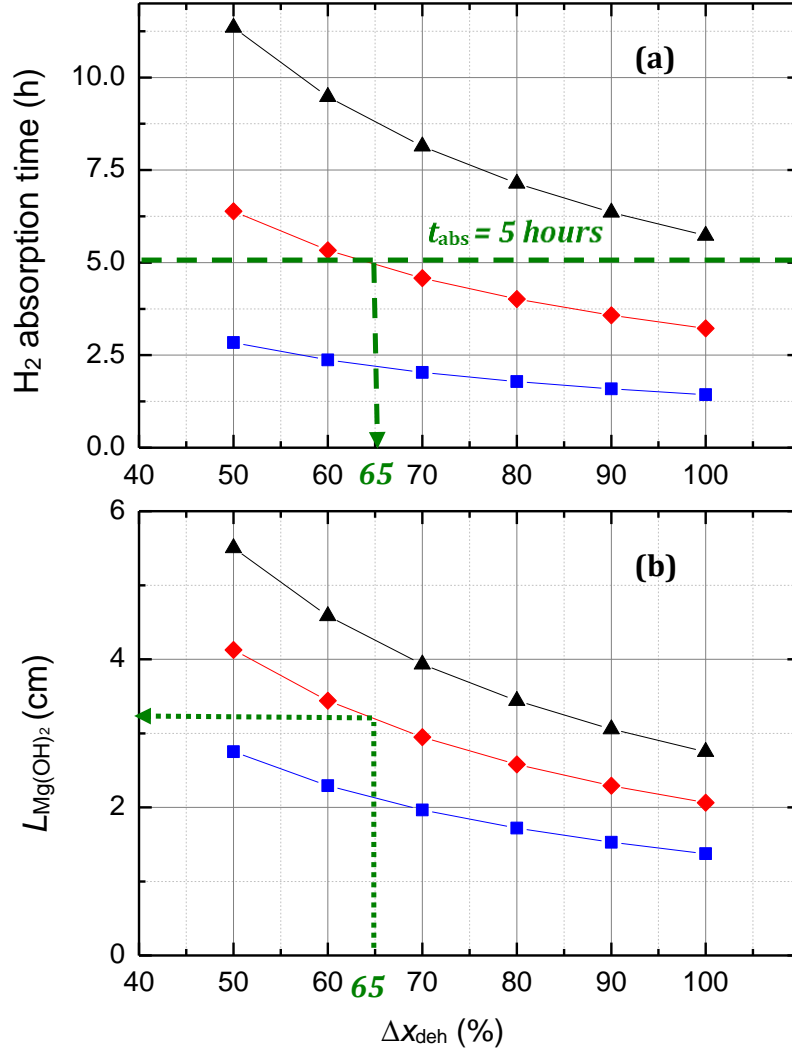
Fig. 4. Dependence of (a) the H_2 absorption time and (b) the thickness of $Mg(OH)_2$ media on the dehydrated fraction of water vapor, Δx_{deh} for three selected thicknesses of MgH_2 bed - Case of rectangular geometry.

4.1.2. Case of cylindrical geometry of Mg/MgH_2 and $MgO/Mg(OH)_2$ beds - Magnesium hydroxide as EM8 pellets

In cylindrical geometry, the hydrogen absorption time, t_{abs} and the radius of $Mg(OH)_2$ media, $R_{Mg(OH)_2}$ are calculated as function of the dehydrated fraction of water vapor, Δx_{deh} ranging from 50% to 100% for three selected magnesium hydride radius, R_{Mg} =1 cm, 2 cm and 3 cm while assuming a radius of the inner tube, R_1 equal to 1/4 R_{Mg} (see Fig. 3(b)). As can be seen from Fig. 5(a), (b), the evolution of t_{abs} and $R_{Mg(OH)_2}$ are qualitatively similar to those in case of rectangular geometry (Fig. 4(a), (b)). However, for this cylindrical configuration, calculation results show that the selection of a radius, R_{Mg} of 2 cm or less can ensure the filling of the hydrogen storage media in a time interval less than 5 hours (see the green dashed line in Fig. 5(a)). For example, by setting R_{Mg} equal to 2 cm, t_{abs} and $R_{Mg(OH)_2}$ can vary from 3 to 5 hours and from 3.75 cm to 5 cm, respectively, depending on the dehydrated fraction of water vapor, Δx_{deh}.
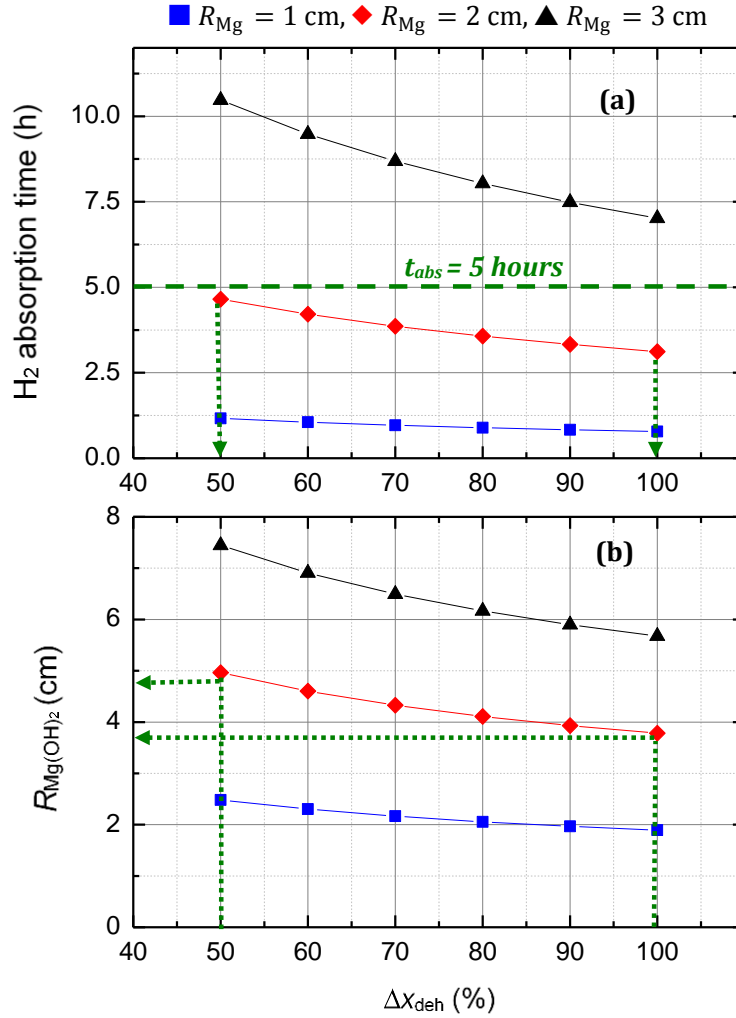
Fig. 5. Dependence of the H$_2$ absorption time (a) and the thickness of Mg(OH)$_2$ media (b) on the dehydrated fraction of water vapor, Δx_{deh} for three selected thicknesses of MgH$_2$ bed - Case of cylindrical geometry.

4.1.3. Discussion and requirement for the optimization of thermochemical storage

For both, rectangular and cylindrical geometries, hydrogen absorption times much less than 5 hours could be achieved for very thin thicknesses of MgH$_2$ and Mg(OH)$_2$ media as can be seen from Figs. 4(a) and 5(a). However, the design of MgH$_2$ reactor based on such geometrical characteristics would require a large number of either, rectangular cells or cylindrical tubes to store the amount of hydrogen required by the targeted application. This would make the MgH$_2$ storage system based on Mg(OH)$_2$ heavier and bulkier and increase its total cost. One way to address this issue is to improve the thermal conductivity of the magnesium hydroxide bed so that better heat exchange between the hydrogen and heat storage media could be achieved. This aspect is investigated in the next section while focusing on the cylindrical geometry. The choice of this reactor configuration allows the use of MgH$_2$ and Mg(OH)$_2$ in pelletized form while benefiting from their high thermal conductivities in radial direction, as well as a uniform distribution of their operating pressures.

4.2. Dependence of the H$_2$ absorption time on Mg(OH)$_2$ properties

Three different types of magnesium hydroxide material are selected here to analyze and compare the effect of their densities and thermal conductivities on the performance of

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hydrogen absorption process. Kato et al. [32] developed a composite material, named EM by drying a mixture of $Mg(OH)_2$ powder, expanded graphite (EG) and water, and took advantage of its mold-ability property to propose its use as small pellets or a block matching the dimensions of the container. With an optimized mixing mass ratio, r_{mix} of 8/9, this two shaped materials are referred here as EM8 pellets and EM8 block. Despite the high thermal conductivity of EG, their measured thermal conductivities are still low compared to the one of MgH_2 used for calculations (see Tables 1 and 2). Thus, a third alternative is considered where loose powder of pure $Mg(OH)_2$ material is filled into a metal matrix foam (e.g. based on aluminum). The properties of the considered media are calculated based on the following expressions

$$\rho_{Mg(OH)_2,eqv} = \varepsilon_{Al.foam}(1 - \varepsilon_{Mg(OH)_2})\rho_{Mg(OH)_2} \tag{6}$$

$$\lambda_{Mg(OH)_2,eqv} = \lambda_{Al.foam} + \varepsilon_{Al.foam}\lambda_{Mg(OH)_2} \tag{7}$$

while assuming a true density, porosity and thermal conductivity of the $Mg(OH)_2$ powder of 2340 kg/m³, 90% and 0.1 W/(m.K), respectively [16]. The same properties of aluminum matrix foam presented in [37] are used for the present calculations and an effective thermal conductivity, $\lambda_{Mg(OH)_2,eqv}$ of 11 W/(m.K) is achieved (see Table 2), comparable to that of magnesium hydride.

The H_2 absorption times and $Mg(OH)_2$ radius of the selected cases are calculated for a minimum dehydrated fraction of water vapor, Δx_{deh} equal to 50% while setting the radius of MgH_2 tube, R_{Mg} at 2 cm. Results are illustrated in Fig. 6.
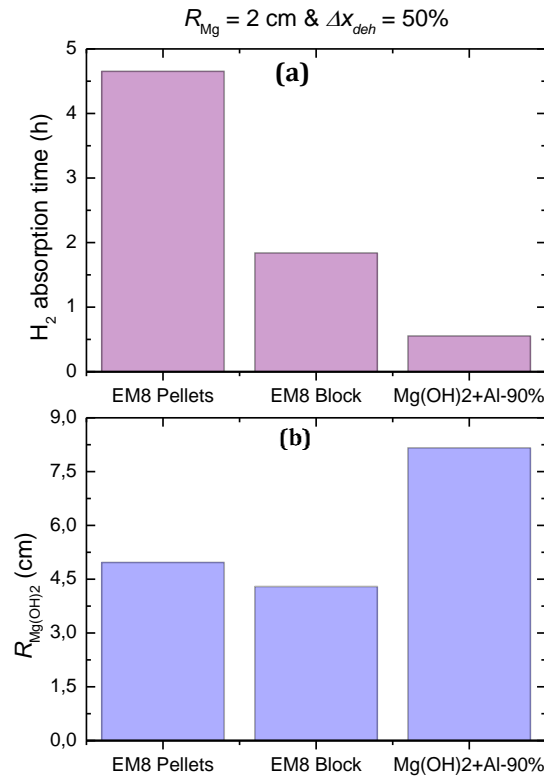

Fig. 6. H_2 absorption time (a) and $Mg(OH)_2$ thickness (b) as function of $Mg(OH)_2$ material properties ($Mg(OH)_2$ as EM8 pellets, $Mg(OH)_2$ as EM8 Block and $Mg(OH)_2$ as loose powder with a porosity of 90% filled in an Al matrix foam), calculated for a dehydrated fraction of water vapor, Δx_{deh} of 50 % and a MgH_2 bed thickness of 2 cm, in case of cylindrical geometry.

From these histograms, it is obvious that a significant reduction of H$_2$ absorption time is obtained with the improvement of Mg(OH)$_2$ thermal conductivity. By increasing $\lambda_{\mathrm{Mg(OH)_2}}$ by a factor of 2 and 20, it would be possible to store hydrogen in time intervals of about 2 hours and half an hour, respectively. Better results could be even obtained for higher dehydrated fractions, Δx_{deh}. Regarding the thickness of Mg(OH)$_2$ media, a slight decrease of $R_{\mathrm{Mg(OH)_2}}$ is obtained when the material density is increased by 30% in case of EM8 pellets and EM8 block (compare materials densities in Table 2). However, the use of Mg(OH)$_2$ as loose powder with a porosity of 90% lowers its density to 209 kg/m^3. Thus, more amount of Mg(OH)$_2$ material is required and its radius is almost the double of $R_{\mathrm{Mg(OH)_2}}$ in case of EM8 block and *eight times* R_{Mg}. It follows from these results that there is a trade-off between the improvement of hydrogen absorption time and the size of the MgH$_2$/Mg(OH)$_2$ combination tube if Mg(OH)$_2$ material is filled into an aluminium matrix foam.

4.3. Dependence on the operational conditions

In addition to the geometric characteristics and material properties, the hydrogen absorption time also depends on the operational conditions of pressure and temperature. For magnesium hydride, the storage of hydrogen at a given pressure, $P_{\mathrm{H_2,abs}}$ is accompanied by a heat release (Q_{abs}) due to the exothermic nature of the reaction. As a result, the hydride bed temperature increases and reaches the equilibrium, $T_{\mathrm{eq,abs}}$. Similarly, during the endothermic dissociation of magnesium hydroxide, the dehydration temperature of the packed Mg(OH)$_2$ bed, $T_{\mathrm{eq,dehy}}$ depends on the water vapor pressure, $P_{\mathrm{H_2O,dehy}}$ [19]. Thus, by manipulating the hydrogen absorption pressure and the water vapor pressure, different temperature gradients between the hydride and hydroxide media could be obtained. Here, the hydrogen absorption time is calculated for $T_{\mathrm{eq,abs}}$ and $T_{\mathrm{eq,dehy}}$ ranging from 350 $^{\mathrm{o}}$C to 400 $^{\mathrm{o}}$C and from 270 $^{\mathrm{o}}$C to 340 $^{\mathrm{o}}$C, respectively (see Eqs. 4 and 5). The properties of magnesium hydroxide as EM8 pellets with a dehydrated fraction of water vapor, Δx_{deh} of 50% are used for this calculation. The radius of magnesium hydride tube is set at 2 cm, corresponding to a magnesium hydroxide tube radius of 4.96 cm.

Figure 7 shows the evolution of the hydrogen absorption time as function of the temperature gradient ($T_{\mathrm{eq,abs}} - T_{\mathrm{eq,dehy}}$). As expected, it follows that larger temperature gradients between the hydrogen storage media and the heat storage media result in shorter hydrogen absorption times. For example, by setting $T_{\mathrm{eq,dehy}}$ at 340 $^{\mathrm{o}}$C and increasing $T_{\mathrm{eq,abs}}$ from 350 $^{\mathrm{o}}$C to 400 $^{\mathrm{o}}$C, the hydrogen absorption time is reduced from about 14 hours to two hours and a half (see blue dotted line in Fig. 7). This MgH$_2$ equilibrium temperature range corresponds to an absorption pressure, $P_{\mathrm{H_2,abs}}$ varying from 6.2 bar to 18 bar. However, as discussed earlier, the practical absorption pressure, $P_{\mathrm{H_2,abs}}$ for the magnesium hydride tank is 10 bar. Thus, it is more suitable to set the hydride temperature at 370 $^{\mathrm{o}}$C and vary $T_{\mathrm{eq,dehy}}$ (Curve with blue triangle symbol in Fig. 8). Kato et al. [26,28] showed that reasonable dehydration rates and good cyclic ability at medium-temperatures ranging from 270 $^{\mathrm{o}}$C to 300 $^{\mathrm{o}}$C and dehydration pressures, $P_{\mathrm{H_2O,dehy}}$ less than 1 bar, can be achieved when Mg(OH)$_2$ is mixed with optimized ratios of lithium bromide (LiBr) and expanded graphite (EG). For this same range of $T_{\mathrm{eq,dehy}}$, a hydrogen absorption time of less than 2 hours can be achieved, which is comparable to the case of using EM8 block (compare to Fig. 6).
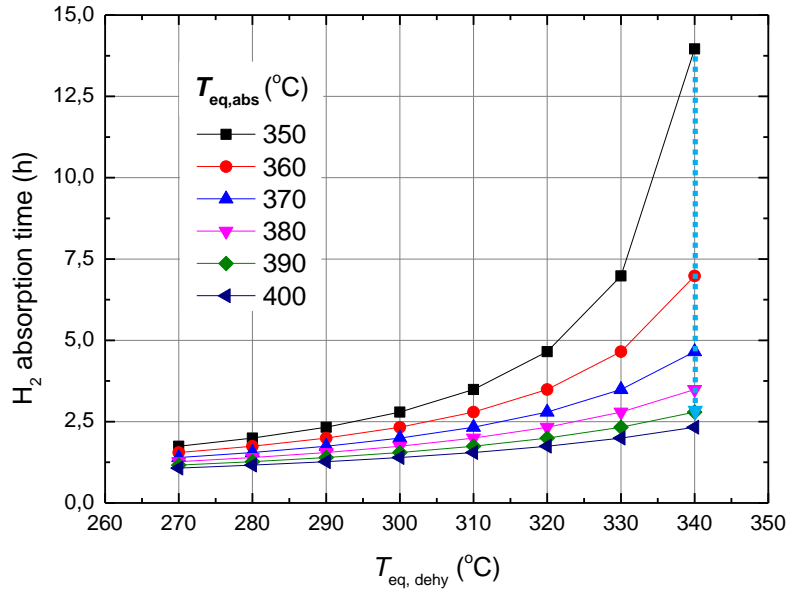
Fig. 7. Dependence of the H_2 absorption time on the equilibrium H_2 absorption temperature, $T_{eq,abs}$ of MgH_2 system and the equilibrium dehydration temperature, $T_{eq,dehy}$ of $Mg(OH)_2$ system.

4.4. Considerations for hydrogen desorption process

The same analytical formulation described above for hydrogen absorption can be used for the evaluation of hydrogen desorption time. In this case, the desorption pressure, $P_{H_2,des}$ dictates the minimum temperature to be reached in the magnesium hydride bed. For fuel cell supply applications, hydrogen should be released at pressure greater than or equal to 1 bar, which corresponds to equilibrium desorption temperature close to 300 ºC (see MgH_2 van't Hoff diagram in Fig. 1). Accordingly, the hydration of magnesium oxide should occur at higher temperature to ensure the transfer of its reaction heat from the heat storage media to the hydrogen storage media as explained in Section 2.2. In other words, a water vapor pressure, $P_{H_2O,hyd}$ above 3.6 bar is required for the hydration of magnesium oxide as it can be seen from the theoretical $Mg(OH)_2$ van't Hoff diagram presented in Fig. 1. This pressure can, e.g., be ensured by the heat loss of a HT-PEMFCs or even the use of water vapor released during its operation, leading then to a closed system.

Experiments of Kato et al. [32] on MgO hydration reaction in EM8 block showed that at 3.61 bar, hydration was completed within one hour and the reaction was controlled by heat transfer. However, the measured temperature of the packed bed was approximatively 220-230 ºC, which is much lower than the one calculated from the theoretical van't Hoff diagram at the same hydration pressure (310 ºC at 3.61 bar). Such a result suggests the presence of a hysteresis between the hydration and dehydration reactions and further experimental studies for the $MgO/Mg(OH)_2$ material are required to indicate which hydration pressure will be needed for the desorption of hydrogen in an application.

5. Comparison with existing technology

After the general feasibility of the adiabatic hydride storage reactor based on Magnesium hydride/ Magnesium hydroxide as well as first geometric studies have been shown, in this section, the new system is compared to state of the art systems with regard to general system properties as well as to H_2 uptake performance. As reference

system, the magnesium hydride storage reactor in combination with a PCM has been used [8].

5.1. System characteristics

System weight

For the reference study by Garrier et al. [8], $Mg_{69}Zn_{28}Al_3$ has been used as PCM to store the heat of reaction in the MgH_2 reactor developed. The choice of this eutectic metal alloy is based on its attractive thermodynamic and thermal properties allowing better thermal exchange with MgH_2 media, so that acceptable time intervals for hydrogen absorption and desorption have been achieved in case of stationary applications. However, the use of $Mg_{69}Zn_{28}Al_3$ results in a drastic decrease of the gravimetric capacity of MgH_2 system. Indeed, starting with a gravimetric capacity of 6.3 wt% for the MgH_2 pellets, it is lowered to 0.315 wt.% for the whole storage system since a mass of *126 kg* of PCM is required to store/release the heat of reaction of *9.9 kg* of MgH_2 pellets [8].

For the new reactor concept investigated in this study, $Mg(OH)_2$ is used as thermochemical heat storage media to store the heat of reaction released during the absorption of hydrogen. The amount of heat to be stored in $Mg(OH)_2$ dehydration reaction is given by $Q_{abs} = \Delta x \cdot m_{Mg(OH)_2} \cdot \Delta H_{Mg(OH)_2}/M_{Mg(OH)_2}$, where Δx, $m_{Mg(OH)_2}$, $M_{Mg(OH)_2}$ and $\Delta H_{Mg(OH)_2}$ are the reacted fraction of water vapor in 1, the mass in kg, the molecular weight of $Mg(OH)_2$ in $kgmol^{-1}$ and the enthalpy of reaction in $Jmol^{-1}$, respectively. Based on the same mass of MgH_2 contained in the H_2 storage system using latent heat storage and its corresponding gravimetric capacity, the mass of $Mg(OH)_2$ required to remove the reaction heat generated during hydrogen absorption is

$$m_{Mg(OH)_2} = \left(w_t \cdot m_{MgH_2} \cdot \Delta H_{MgH_2}/M_{H_2}\right)/\left(\Delta x \cdot \Delta H_{Mg(OH)_2}/M_{Mg(OH)_2}\right) \qquad (8)$$

where w_t, m_{MgH_2} and ΔH_{MgH_2} are the gravimetric capacity in wt.%, the mass in kg and the enthalpy of MgH_2 in $Jmol^{-1}$ respectively and M_{H_2} is the molecular weight of hydrogen in $kgmol^{-1}$.

Even in a worst case scenario, where only Δx = 50% of the water vapor reacts, this results in a mass, $m_{Mg(OH)_2}$ of *31.6 kg* using data listed in Tables 1 and 2. This represents a *quarter* of $Mg_{69}Zn_{28}Al_3$ mass used in [8] and it refers to a gravimetric capacity of still approx. 1.5 wt.%. Even though magnesium hydride is mainly used for stationary applications where achieving low system weight is not considered as high priority, it is obvious that the development of MgH_2 reactor using $Mg(OH)_2$ as thermochemical storage media would result in a considerable improvement of the gravimetric capacity of the whole storage system.

Furthermore, it can also be noted that the overall gravimetric capacity of the $MgH_2+Mg(OH)_2$ with 1.5 wt% is still in the range or even better than the capacity of classical metal hydride materials like $LaNi_5$ with approx. 1.3 wt.% [38].

System cost

For the $Mg(OH)_2$ material, the required mass is not only reduced to one quarter of the mass for the PCM, but also the cost per kg is significantly lower than for the PCM. Therefore, it is obvious that the system cost of the presented storage reactor is much lower. For instance, with a commercial price of 0.2 – 1 $/kg [39], the storage reactor based on the $Mg(OH)_2$ will have extra material costs of approx. 20 to 30 $. In contrast, as the price of magnesium (Mg), Zinc (Zn) and aluminum (Al) materials is approximately between 2 and 3 $/kg [40], the material cost for the PCM storage are 250 to 375 $! Thus,

even though the reactor design for the $Mg(OH)_2$ material might be more complex, there exists a significant potential benefit of the new adiabatic MgH_2 reactor concept based on thermochemical heat storage.

System reliability and complexity

When looking at the system complexity, it is obvious that the combination of a MgH_2 with the $Mg(OH)_2$ system is more complex than the combination with a PCM. This is mainly due to the required water management for the $Mg(OH)_2$ material. However, as suggested in the operating principle, the integration with a HT-PEMFC can be sufficient to provide the required water for hydrogen desorption.

Furthermore, it is clear that the suggested concept is on a very low technology readiness level at the moment; however, it could also offer an advantage in system complexity: For the PCM, special care has to be taken to avoid cooling down below the melting temperature when storing the heat. In contrast, the $Mg(OH)_2$ system can still operate, even if it was cooled down to room temperature as the heat is stored in the chemical reaction (with a heat capacity that is reduced by the temperature decrease).

Flexibility of the system

Another advantage of the proposed concept is the flexibility of the operational conditions for both, magnesium hydride and magnesium hydroxide reactions. Indeed, for the H_2 storage system based on latent heat storage, the operation temperature of the phase change material is fixed and the driving temperature gradient between the MgH_2 and the PCM needs to be generated by the hydrogen storage material itself by imposing a higher hydrogen absorption pressure than the desorption. In case of MgH_2 reactor based on thermochemical heat storage, the thermochemical material can contribute to the generation of different temperature gradients by varying the condensation and evaporation temperatures, T_c and T_v, respectively. Thus, larger driving temperature gradients between the hydrogen and heat storage media can be achieved and more efficient use of the reaction heat is expected.

5.2. System performance

Complementing the comparison of some general characteristics of the storage reactor, in this section the performance of this new adiabatic hydride reactor with $Mg(OH)_2$ is compared to the PCM-based system from the literature using the identical geometry.

The MgH_2 reactor based on latent heat storage [8] consists of two concentric tubes filled with MgH_2 and PCM and having radius of 7 cm and 14 cm, respectively. It was filled with hydrogen in a time interval of 5 hours. Thus, the same radius of magnesium hydride tube, R_{Mg} equal to 7 cm is selected to recalculate the hydrogen absorption time using the equations presented before. As with this thick inner diameter the heat conductivity of the $Mg(OH)_2$ material gets more and more important, the radius of $Mg(OH)_2$ tube has been calculated for a case where the material is filled into an aluminum matrix foam. Due to the low density of the $Mg(OH)_2$ with 90% of porosity (see Eq. 6), this results also in a very thick radius for this material. In order to address this problem, the $Mg(OH)_2$ porosity, $\varepsilon_{Mg(OH)_2}$ is improved from 90% to 70% in the present calculations resulting in $Mg(OH)_2$ densities ranging from 209 kg/m^3 to 638 kg/m^3 for the same value of thermal conductivity, $\lambda_{Mg(OH)_2,eqv}$ equal to 11 W/(m.K).

Figure 8 shows the resulting absorption time and $Mg(OH)_2$ radius for two values of the dehydrated fraction of water vapor, Δx_{deh} (50% and 80%). From these histograms,

it can be seen that a comparable performance of the developed MgH$_2$ reactor based on latent heat storage could be achieved when magnesium hydroxide has a thermal conductivity of 11 W/(m.K) and a porosity of 70%. The corresponding density is equivalent to that of pelletized pure Mg(OH)$_2$ studied by Kato et al. [32]. With such properties and for Δx_{deh} of 80%, the radius of the Mg(OH)$_2$ tube is equal to 14 cm, same as the radius of PCM tube for the MgH$_2$ tank developed by Garrier et al. [8].

From a practical perspective, it is tricky to achieve such a density by filling the Mg(OH)$_2$ material into an aluminum matrix foam. However, the obtained results are useful since they allow to determine the optimum range of density and thermal conductivity of Mg(OH)$_2$ media so that comparable hydrogen storage performance to the case of MgH$_2$ based on latent heat storage could be achieved while using a less weight and cost thermochemical material, as discussed before.
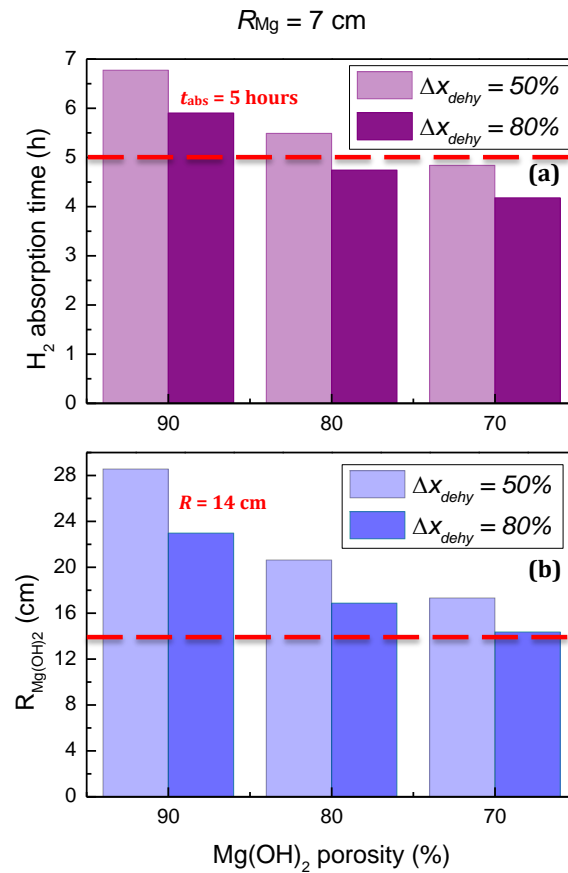

Fig. 8. H$_2$ absorption time (a) and Mg(OH)$_2$ thickness (b) as function of Mg(OH)$_2$ porosity, calculated for a dehydrated fractions of water vapor, Δx_{deh} of 50 % and 80 %, and a MgH$_2$ bed thickness of 7 cm, in case of cylindrical geometry.

6. Conclusions

In this paper, the feasibility of a new adiabatic metal hydride reactor concept using a thermochemical heat storage material to store the absorption reaction heat has been studied. Magnesium hydride and magnesium hydroxide have been identified as suitable reference materials to be combined based on their operating temperatures range. In addition, both of them are promising materials in terms of cost, availability and storage capacity.

The performance of the hydrogen loading process for this new reactor concept has been evaluated based on an analytical formulation of the hydrogen absorption time as function of the geometrical characteristics of the two storage media, their properties and their operating conditions. The analytical formulation was applied for a pelletized magnesium hydride media and three types of magnesium hydroxide material: EM8 pellets, EM8 block and pure $Mg(OH)_2$ filled in an aluminum matrix foam, to determine materials and systems parameters for different geometries and material parameters.

The main results arising from these calculations are that short hydrogen absorption times (less than 5 hours) could be achieved for a reference MgH_2 pellet and thin $Mg(OH)_2$ media thickness, and the improvement of the thermal conductivity of magnesium hydroxide bed enables the use of thicker hydrogen and heat storage media for the same absorption time intervals.

The comparison with state of the art MgH_2 tank using PCM showed that a comparable hydrogen absorption time and geometric characteristics could also be achieved if the effective $Mg(OH)_2$ thermal conductivity is equal to the one of pelletized MgH_2 ($\sim$10 W/(m.K)) with a density of 638 kg/m^3. Moreover, the possibility to adjust the gas pressures independently allows for more flexible operations. By adjusting the water vapor pressure and the hydrogen ab- and desorption pressures, faster dynamics of the system could be reached since higher gradient between the equilibrium temperatures of the two hydrogen and thermochemical heat storage media can be achieved.

Furthermore, with such a reactor design, the required mass of $Mg(OH)_2$ is reduced by a factor of 4 in comparison to the mass of phase change material used in MgH_2 reactor based on latent heat storage. This will result in an adiabatic hydrogen storage system of lower cost (factor 10) and higher gravimetric capacity compared to the one using phase change material, potentially opening then the way to its integration in applications other than stationary sector.

Acknowledgements

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Nomenclature

Materials	
Al	Aluminum
EG	Expanded graphite
Mg/MgH_2	Magnesium / Magnesium hydride
$MgO/Mg(OH)_2$	Magnesium oxide / Magnesium hydroxide
$Mg_{69}Zn_{28}Al_3$	Metallic PCM

Parameters	
L	Thickness of layer in m
m	Mass in kg
M	molecular weight in $kg.mol^{-1}$
P	Pressure in MPa
Q	Heat in kJ
r_{mix}	Mixing ratio of graphite and MgO
R	Radius in m
t	Time in hour
T	Temperature in °C
w_t	Transformed weight fraction of metal hydride in %
Δx	Reacted fraction of water vapor in 1
ΔH	Reaction enthalpy in $kJ.mol^{-1}.K^{-1}$
λ_i	Thermal conductivity of component i
ε	Porosity
ρ	Density in $kg.m^{-3}$

Subscripts	
abs	Absorption
c	Condensation
dehy	Dehydration
des	Desorption
eq	Equilibrium
eqv	Equivalent
e	Evaporation
hy	Hydration

Table

Parameter	Symbol	Value
Equilibrium absorption temperature (ᵒC)	$T_{eq,abs}$	370
Reaction enthalpy (kJ/mol)	ΔH_{Mg}	75
Density (kg/m³)	ρ_{Mg}	1945
Porosity (1)	ε	0.44
H_2 storage capacity (%)	w_t	5.94
Thermal conductivity (W/(m.K))	λ_{Mg}	10
Molecular weight of H_2 (kg/mol)	M_{H_2}	0.002

Table 1 – Properties of MgH₂ used in analytical analysis [36]

Parameter	Symbol	Value		
		EM8 Pellets	EM8 Block	Mg(OH)$_2$+Al foam
Equilibrium dehydration temperature (°C)	$T_{eq,dehy}$	340		
Reaction enthalpy (kJ/mol)	$\Delta H_{Mg(OH)_2}$	81		
Density (kg/m³)	$\rho_{Mg(OH)_2}$	714	1022	209.32, 425.88, 638.82
Porosity	$\varepsilon_{Mg(OH)_2}$	-	-	90%, 80%, 70%
Dehydrated fraction of water vapour (%)	Δx_{deh}	50 - 100		
Mixing ratio	r_{mix}	8/9	8/9	—
Thermal conductivity (W/(m.K))	$\lambda_{Mg(OH)_2}$	0.55	1.2	11
Molecular weight of Mg(OH)$_2$ (kg/mol)	$M_{Mg(OH)_2}$	0.058		

Table 2 – Properties of Mg(OH)$_2$ used in analytical analysis [16, 32]

Fig. 1. Pressure-Temperature phase diagrams for Mg/MgH_2 and $MgO/Mg(OH)_2$ systems.
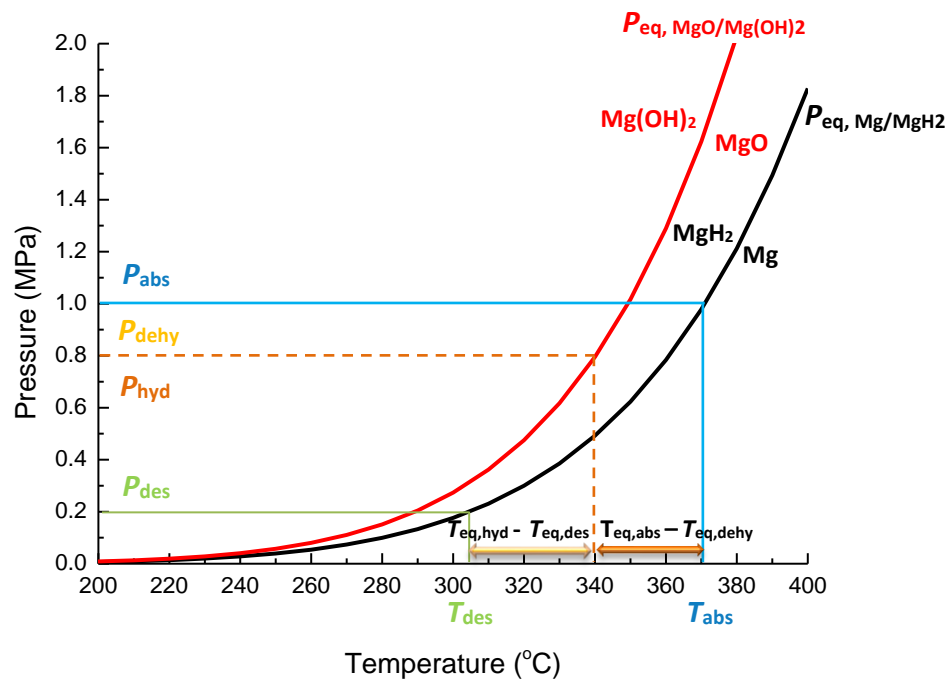
Fig. 2. Operating principle of magnesium hydride reactor using magnesium hydroxide as heat storage media: (a) Absorption of H_2 /Dehydration of $Mg(OH)_2$/Condensation of H_2O, and (b) Desorption of H_2 /Hydration of MgO/Evaporation of H_2O.
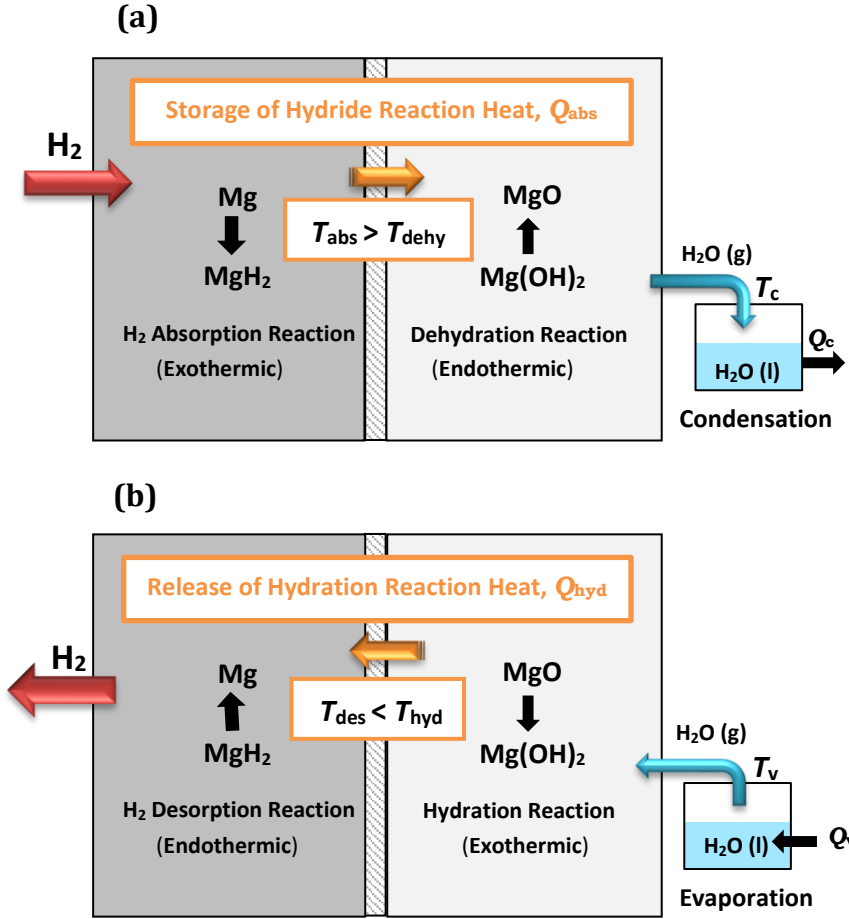
Fig. 3. Schematic of the used geometry in the analytical study showing the hydrogen absorption front and the $Mg(OH)_2$ dehydration front in (a) rectangular and (b) cylindrical coordinates.
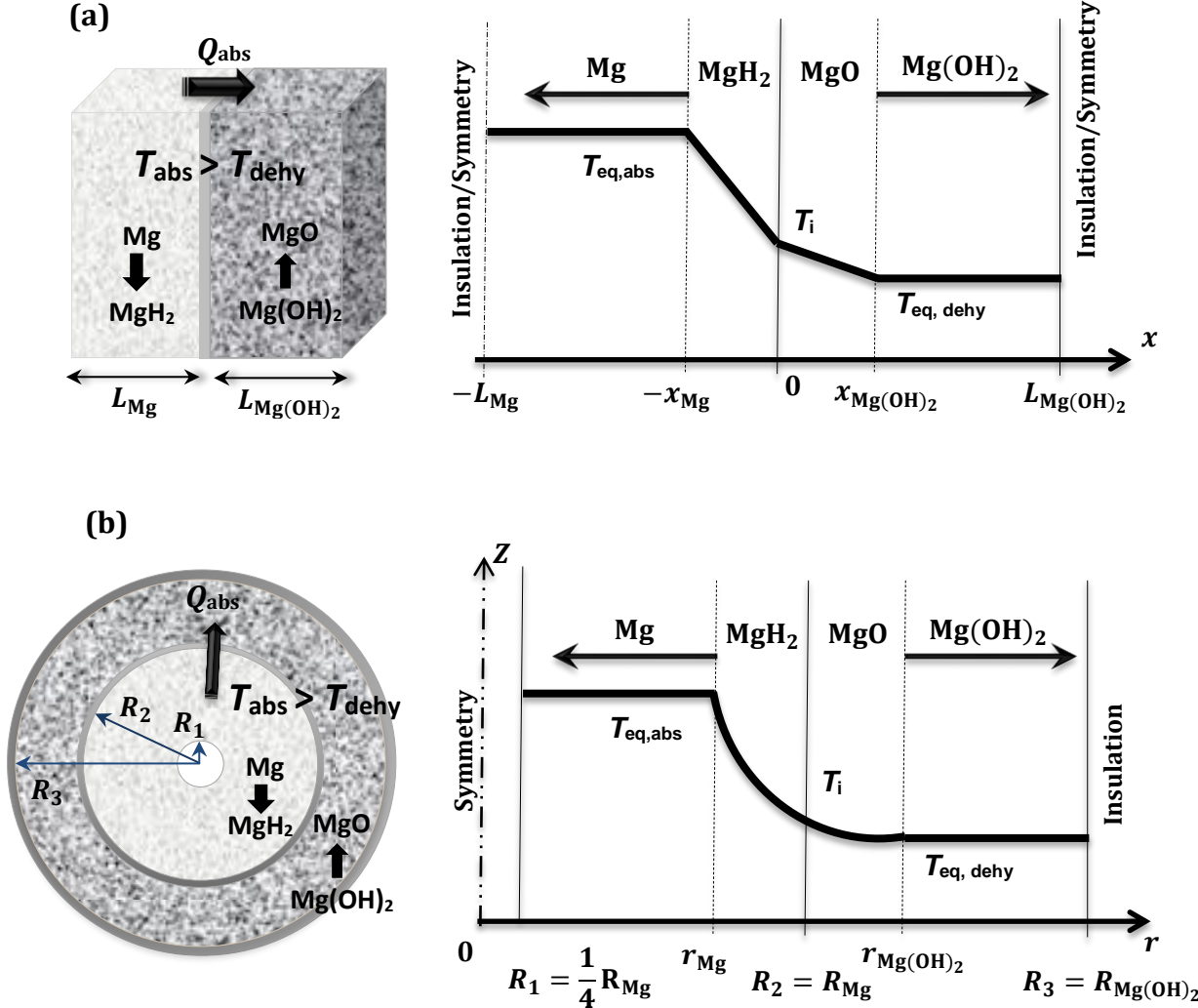
Fig. 4. Dependence of (a) the H_2 absorption time and (b) the thickness of $Mg(OH)_2$ media on the dehydrated fraction of water vapor, Δx_{deh} for three selected thicknesses of MgH_2 bed - Case of rectangular geometry.
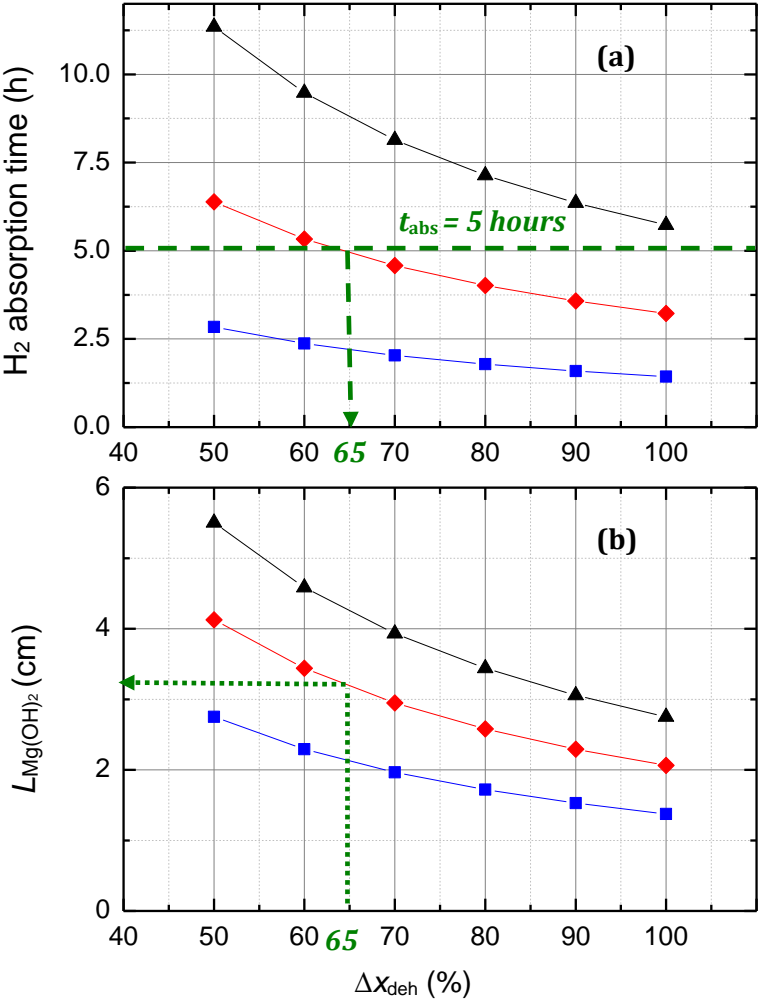
Fig. 5. Dependence of (a) the H_2 absorption time and (b) the thickness of $Mg(OH)_2$ media on the dehydrated fraction of water vapor, Δx_{deh} for three selected thicknesses of MgH_2 bed - Case of cylindrical geometry.
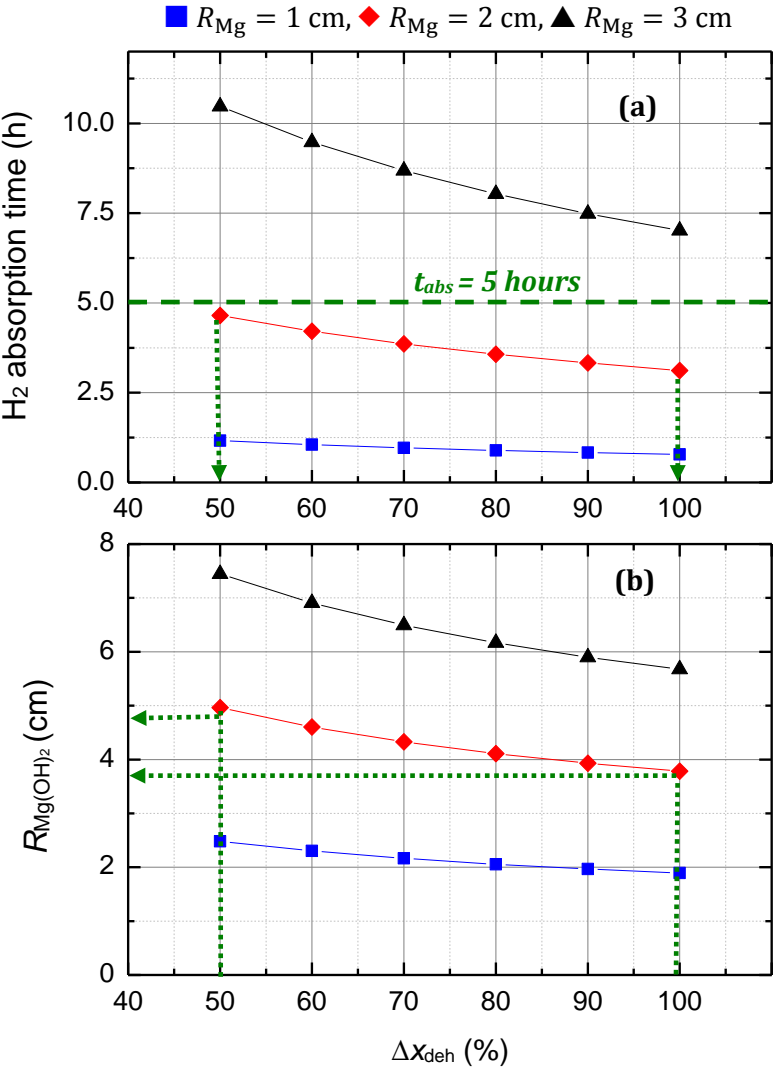
Fig. 6. H_2 absorption time (a) and $Mg(OH)_2$ thickness (b) as function of $Mg(OH)_2$ material properties ($Mg(OH)_2$ as EM8 pellets, $Mg(OH)_2$ as EM8 Block and $Mg(OH)_2$ as loose powder with a porosity of 90% filled in an Al matrix foam), calculated for a dehydrated fraction of water vapor, Δx_{deh} of 50 % and a MgH_2 bed thickness of 2 cm, in case of cylindrical geometry.
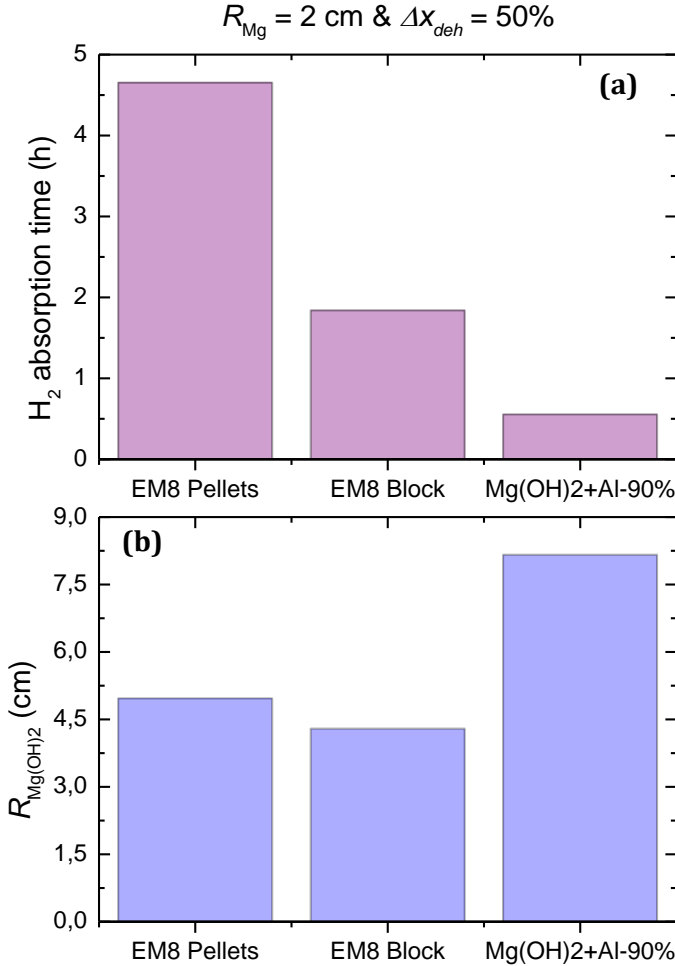
Fig. 7. Dependence of the H_2 absorption time on the equilibrium H_2 absorption temperature, $T_{eq,abs}$ of MgH_2 system and the equilibrium dehydration temperature, $T_{eq,dehy}$ of $Mg(OH)_2$ system.

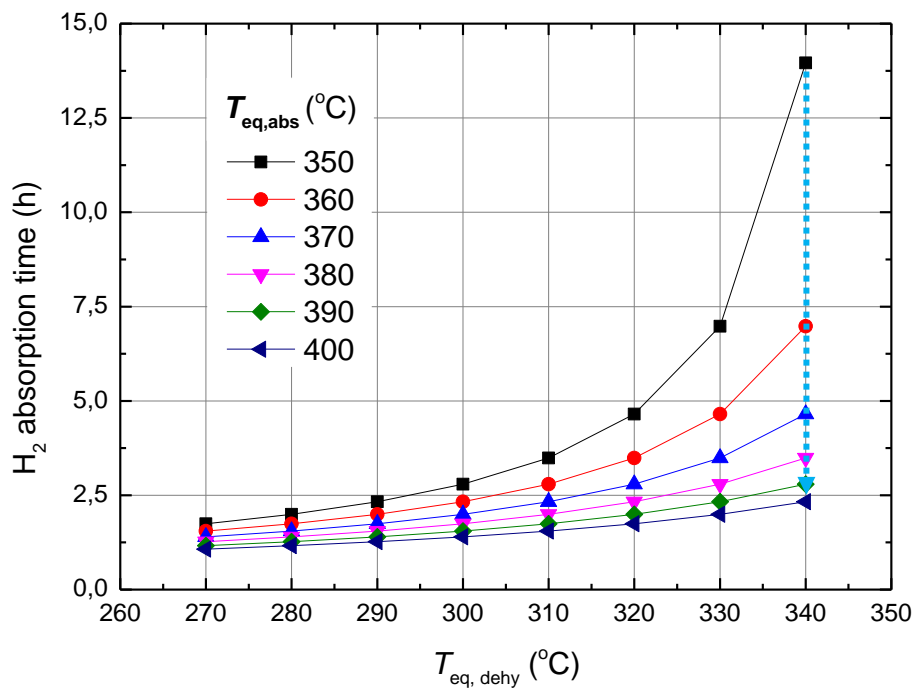**Fig. 8.** H$_2$ absorption time (a) and Mg(OH)$_2$ thickness (b) as function of Mg(OH)$_2$ porosity, calculated for a dehydrated fractions of water vapor, Δx_{deh} of 50 % and 80 %, and a MgH$_2$ bed thickness of 7 cm, in case of cylindrical geometry.