Modeling and Optimization of a Mg – Metal Hydride Rectangular Tank at the Hydriding Process

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Abstact.: Hydrogen storage can be considered as a key factor in the development of hydrogen economy. Hydrogen storage in a magnesium hydride MgH_2 is a very promising technique for numerous of reasons. Magnesium is abundant, relatively cheap, life – friendly , weight storage capacity of 7.6% and low price of Mg metal. A simulation work is presented in order to study the absorption kinetics of a Mg – metal hydride tank. A comparison is also made between two different tanks, a perforated rectangular tank and a conventional rectangular tank, in order to understand the geometrical reliance of the hydrogen storage.

1.Introduction: Using a metal hydride as a material for hydrogen storage is a novel, alternative way for energy application [1]. The metal hydride has the absolute hydrogen quantity which can bear at the material temperature condition and has the property of the chemical reaction which can absorb and desorb hydrogen according to the mutual relations with the surrounding hydrogen pressure [2]. The temperature and supplied pressure can be easily controlled during the cycling process of hydrogenation and dehydrogenation and the fully understanding of the reaction mechanisms is very important for the proper design of relevant hydrogen storage units [3]. It is difficult to predict accurately the physical phenomena occurring in the bed only by using the experimental approaching method. Thus, a numerically approaching method is necessary to make up for the weak points of experimental study and to fully understand the hydrogen reaction and heat, mass and momentum transfer mechanisms in the metal hydride bed.

So the differential equations which describe energy, mass and momentum must be solved [4]. This is performed by using the COMSOL Multiphysics software. The aim of such simulations is to understand how different reactor configurations and operating characteristics affect the absorption process. In the present study we considered two different reactor configurations: the first reactor (BED-1) is a rectangular metal hydride bed containing powdered Mg, while the second tank (BED-2) has holes perpendicular to its large surface, also containing Mg. Mg metal hydride is considered a very potential material for hydrogen storage and over the past few years a number of research has been made [5 - 9]. The hydriding reaction between Mg and hydrogen occurs in the temperature range of 250-3200 degC and has very endothermic characteristics. The comparison of the hydriding kinetics in two different metal hydride beds (BED- 1, BED-2) is studying, aiming to find out the best conditions of hydrogen absorption by Mg.

2. **Numerical model**. The geometry of the model is seen in Figure 1, and consists of a perforated rectangular metal hydride and a conventional metal hydride.
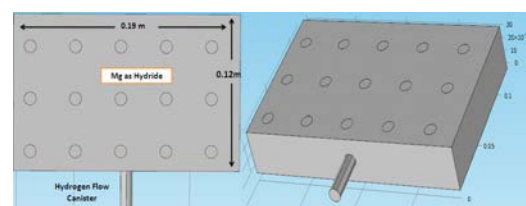

Figure 1. The geometry of the hydride tank

In order to simplify the model, some assumptions has been made. The main assumptions considering for developing the model are the following:

The media (metal and hydrogen) are in local thermal equilibrium (the gas temperature is the same as of the solid temperature)

The solid phase is isotropic and has a uniform porosity

Hydrogen is treated as an ideal gas, from a thermodynamic point of view.

The effect of hydrogen concentration on the variation of equilibrium pressure is negligible (Van't Hoff law)

The governing equations, consist of energy, mass and momentum conservation which described by partial differential equations, and some other equations that describe the kinetics of absorption and desorption. The model describes also the diffusion through the hydride bed, by using the Darcy's law and taking into consideration the kinetics of absorption as a function of the difference between the local and equilibrium temperature.

2.1 Energy equation

Assuming thermal equilibrium between the hydride powder and hydrogen, a single energy equation is solved instead of separate equations foe both solid and gaseous phases.

$$(\rho \cdot Cp)_e \cdot \frac{\partial T}{\partial t} + (\rho_g \cdot Cp_g) \cdot \vec{v}_g \cdot \nabla T$$
$$= \nabla \cdot (k_e \cdot \nabla T) + m \cdot (\Delta H - T \cdot (Cp_g - Cp_s))$$

(1)

Considering only parallel heat conduction in solid and gas phases, there are the following expressions for specific heat and thermal conductivity respectively:

$$(\rho \cdot Cp)_e = (\varepsilon \cdot \rho_g \cdot Cp_g) + ((1-\varepsilon) \cdot \rho_s \cdot Cp_s)$$
(2)

$$k_e = \varepsilon \cdot k_g + (1-\varepsilon) \cdot k_s$$

(3)

Both the equations (2) and (3) are expressed as porosity – weighted functions of the hydrogen – gas and the solid – metal phases.

2.2 Hydride mass balance

For the solid, a mass conservation equation is considered. $(1-\varepsilon) \cdot \dfrac{\partial(\rho_s)}{\partial t} = -m$ (4)

2.3 Hydrogen mass balance

The mass conservation for the gas is considered as:

$$\varepsilon \cdot \frac{\partial(\rho_g)}{\partial t} + div(\rho_g \cdot \vec{v}_g) = -m$$

(5)

2.4 Momentum equation

The gas velocity can be expressed using Darcy's law. By neglecting the gravitational effect, the equation is the above:

$$\vec{v}_g = -\frac{K}{\mu_g} \cdot grad(\vec{P}_g)$$

(6)

Where K is the permeability of the solid and μ_g is the dynamic viscosity of gas. The solid permeability is given by the Kozeny – Carman's equation: $K = \dfrac{dp^2 \cdot \varepsilon^3}{180 \cdot (1-\varepsilon^2)}$ (7)

Assuming that the hydrogen is an ideal gas, from the perfect gas law (ρ_g = (P_g M_g)/(RT)) and considering Darcy's law, the mass conservation equation of hydrogen becomes:

$$\frac{\varepsilon \cdot M_g}{R \cdot T} \cdot \frac{\partial P_g}{\partial t} + \frac{\varepsilon \cdot M_g \cdot P_g}{R \cdot T} \cdot \frac{\partial}{\partial t} \cdot \frac{1}{T} -$$

$$\frac{K}{v_g \cdot r} \cdot \frac{\partial}{\partial r} \cdot \frac{r \cdot \partial P_g}{\partial r} - \frac{K}{v_g} \cdot \frac{\partial^2 P_g}{\partial z^2} = -m$$

(8)

2.5 Kinetic expression

For the absorption and desorption of hydrogen, the following kinetic expressions are used:

$$m = C_a \cdot \exp[-\frac{E_a}{R_g \cdot T}] \cdot \ln[\frac{p_g}{P_{eq}}] \cdot (\rho_{ss} - \rho_s)$$

(9)

$$m = Cd \cdot \exp[-\frac{E_d}{R_g \cdot T}] \cdot (\frac{P_{eq} - p_g}{P_{eq}}) \cdot (\rho_s - \rho_o)$$

(10)

Where (9) is for absorption and (10) for desorption respectively, and m is the source term and used in equations (1), (4), (5), (8). C_a and C_d are pro-exponential constants for absorption and desorption respectively, E_a and E_d are the absorption/desorption activation energy, ρ_{ss} is the saturation density for hydride, and ρ_o is the initial metal hydride density.

2.6 Equilibrium pressure

The equilibrium pressure for the hydrogen, which is the most important parameter which defines if the reaction is going to take place or not, is given by van't Hoff law:

$$\ln P_{eq} = \frac{\Delta H}{R_g \cdot T} - \frac{\Delta S}{R_g}$$

(11)

2.7 Initial and boundary conditions

Initially, gas and solid are at the same temperature. Pressure and hydride density are assumed to be constant.

$$\mathbf{T_s = T_g = T_o} \qquad \mathbf{p_g = p_o}$$
$$\mathbf{\rho_s = \rho_0}$$

Our geometry consists of a rectangular tank, with tubes well distributed perpendicular to the rectangular surface. In Figure 2a is seen the walls of the geometry in where there is a heat flux procedure, and the heat flux condition is set:

$$-\vec{n} \cdot k_e \cdot \nabla T = h \cdot (T - T_f)$$

(12)

The boundaries of the tubes are set with the condition $T = T_0$, where T_0 is the temperature of the cooling air. This is shown in Figure 2b.

The common boundaries between the tube and the perpendicular surface of the reactor has the following condition which corresponds to convective flux. This depicts in Figure 2c.
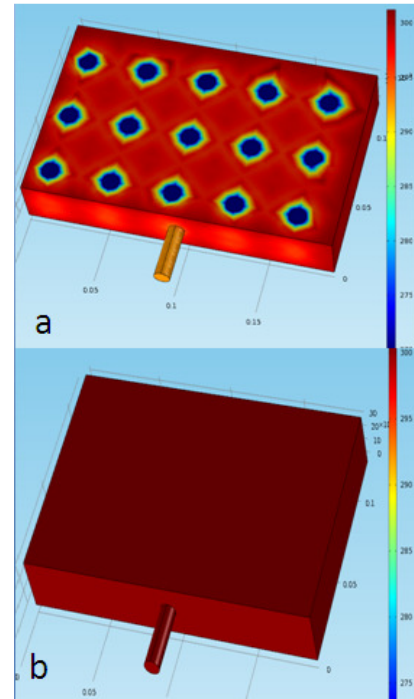

Figure 2. Temperature distribution at the surface of the two tanks

$$-\vec{n} \cdot k_e \cdot \nabla T = 0$$

(13)

Finally, on the hydrogen supply canister (Figure 1), the boundary conditions are: Thermal insulation at the collateral walls,

continuity

$$(-\vec{n} \cdot (k_{eq1} \cdot \nabla T_1 - k_{eq2} \cdot \nabla T_2) = 0)$$ has set at

the common contact area of the supply canister with the tank

3. **Results and discussion**.

Figure 2 shows the temperature evolution at the end of the absorption process for the two tanks. 2a shows the surface temperature distribution of the perforated tank where inside the tubes there is ambient air acting like a cooling fluid with a temperature of 30^0C constant and we observe that the presence of this cooling medium affects the reaction. Further, figure 2b depicts the surface temperature distribution of the conventional tank and there is a difference between the two tanks. The temperature distribution is high homogenous for the conventional tank, where the temperature distribution is totally irregular for the perforated tank.

Figure 3 depicts the temperature – pressure and absorption capacity behavior with time for both the perforated and the conventional rectangular. Figure 3a shows that the presence of the cooling medium indeed affects the absorption procedure. The absorption is a high exothermic reaction and the greater maximum temperature for the perforated rectangular shows that the reaction is more violent there. Further, from figure 3b, we assume that the equilibrium pressure for the perforated rectangular is bigger than the equilibrium pressure for the conventional rectangular (4bar for the perforated and 1.5bar for the conventional). Finally, figure 3c depicts the absorption capacity for both tanks. We assume that the conventional rectangular reaches faster the saturation state at almost $6mol/m^3$. The same saturation value has the perforated rectangular, but slower.

4. **Conclusions**

In this study, a mathematical model describing the absorption of hydrogen was proposed and the comparison of the behavior of two different tanks studied. The results showed that the presence of a cooling medium flow inside the tubes of the perforated tank affects hardly the reaction making more violent but slower. It should be noted that the absorption efficiency was found at $6mol/m^3$ for both cases, which shows the potential for using Mg as a hydrogen storage hydride.
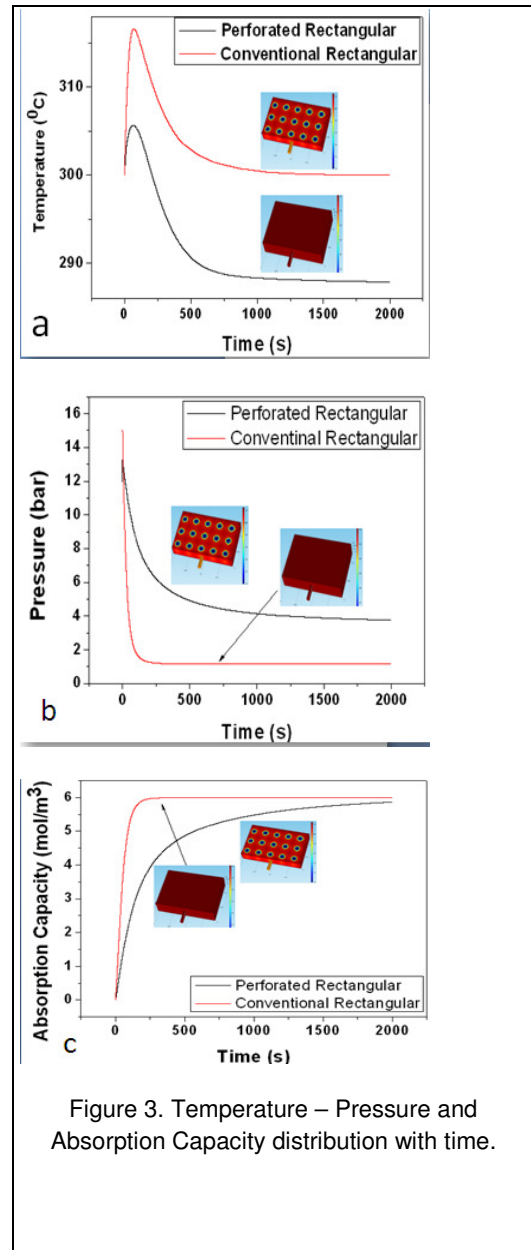

Figure 3. Temperature – Pressure and Absorption Capacity distribution with time.

5. **References.**

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6. Nomenclature

Cp: Specific Heat (J/kgK)
u : Gas Velocity (m/s)
Ea: Absorption Activation Energy (J/mol)
Ed: Desorption Activation Energy (J/mol)
K: Permeability (m^2)
P: Pressure (bar)
T: Temperature (K)
t: Time(s)
R: Gas Global Constant, (8.314 J/molK)
d_p: Particle Size (m)
Greek Symbols
ΔH: Reaction Enthalpy (J/mol)
ε: Porosity
ΔS: Reaction entropy (J/molK)
λ: Thermal Conductivity(W/mK)
μ_g: Dynamic Viscosity (kg/ms)
ρ: Density(kg/m^3)

Subscripts
eq: Equilibrium
g: Gas
m: Metal
o: Initial
s: Solid – Hydride
ss: Saturation