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This document appeared in

Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 4: Storage Systems / Policy Perspectives, Initiatives and Co-operations
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-4
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-654-5

# Design of a Metal Hydride

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## 1 Introduction

Metal hydrides hydrogen storage tanks are chemical reactions based systems that enable the storage of hydrogen. The equation (1) notes the heterogeneous characteristic of the process.

$$M(s)+H_2(g)\leftrightarrow MH_x(s) \quad (1)$$

The process is based on a chemical equilibrium influenced by the reaction materials and the container design factors. The factors that influence the reaction are thermodynamic, kinetic, containers design and materials.

## 2 Thermodynamics

The most important thermodynamic parameters are presented in van't Hoff equation(2) [1-4]

$$Ln P_{eq} = \frac{\Delta S_f^o}{R} - \frac{\left|\Delta H_f^o\right|}{RT} \quad (2)$$

Where $P_{eq}$ is the pressure in the region of equilibrium between phases α - β, $R$ is the ideal gas constant, $\Delta H_f^o$ is the standard variation of enthalpy of formation in the region of phase equilibrium and $\Delta S_f^o$ is the standard variation of entropy in the process of formation and temperature expressed as $T$.

The values of $\Delta H_f^o$ are employed to identify the amount of energy generated or consumed. Allowing the design of the heat management systems. The equations (3) and (4) calculates the heat generated or absorbed by the system, and the heat flow in unit time.

$$Q = m \cdot \Delta H \quad (3)$$

$$\dot{Q} = \dot{m} \cdot \Delta H \quad (4)$$

As seen on the equation(1), the process is reversible. Theoretically both processes behave similar, but in real cases both processes behave different way by effect of the hysteresis. This results in two van't Hoff plots, one for the absorption process and one for the desorption process, as shown in Figure 1.

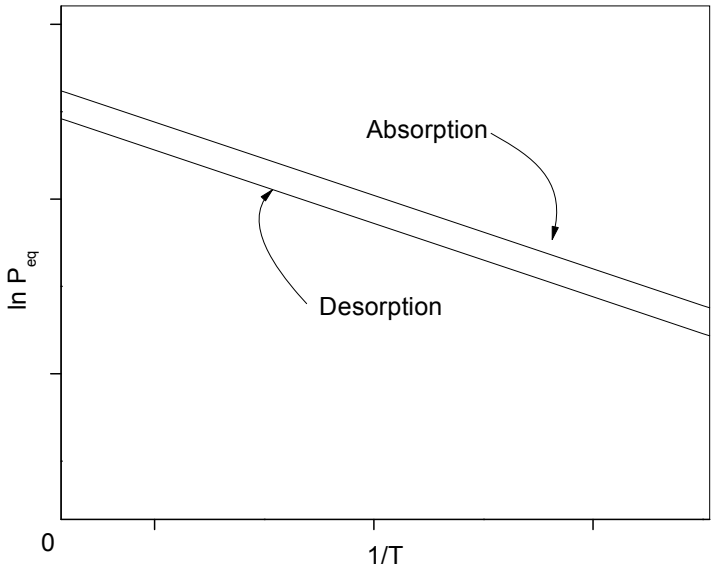


**Figure 1: Van't Hoff plots for the reversible process.**

Hysteresis affects temperature, pressure and composition values. Kinetics can be also affected by hysteresis, but its influence is lower in this case.

The most important thermodynamic variable to design a storage system is the enthalpy of the process, which is obtained from the slope of the equation (2). Considering an hysteresis process there are two solutions the first one is to select the highest value of enthalpy and the second one is to select one enthalpy value for charge and other one for discharge to calculate an optimal heat exchanger.

## 3 Kinetics

The hydrogen supply processes are influenced by the kinetic factors and dead volumes in the systems [5].

The dead volume resulting from porosity. So during the release and filling processes (transitory processes) the system may behave as pressurized storage systems.

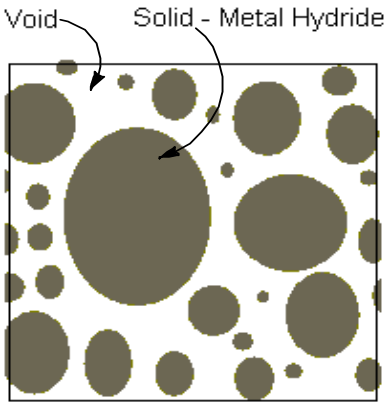


**Figure 2: Porosity of the medium.**

In Figure 2 there is a representation of the interior of the solid porous material. The porosity is at a value of ε = 0.5. It means that half of the container volume is dead volume.

Once steady state is reached, the hydrogen absorption rate is determined by the kinetics of the process. Thus the selection of the total dead volume of the system allow the design the initial flow capabilities of the system. Depending on the required initial flow, the amount of dead volume increase or decrease. Systems internal hydrogen combustion engines require high volumes in short periods of time so that dead space has to be greater.

This transitory flow present the stationary conditions of metal hydrides (before starting discharge). This is because the system was in equilibrium with the hydrogen storage alloy. This pressure is the maximum hydrogen supply pressure. The maximum pressure is just reached in case the metal hydride was in equilibrium before discharge. In case there isn't sufficient time to reach equilibrium, the system will behave dependent on kinetic process.

Although the kinetic processes affects during the entire operation of the system, in the transitory those processes are overlap with the effects of dead volumes previously mentioned. These effects, even getting significantly increase the initial values of discharge flows, do not influence the overall system behaviour.

For the determination of charge and discharge flows and rates a preliminary kinetic analysis has to be done. For this reason it's necessary to analyze the metal hydrides charging and discharging times.

The hydrides kinetic processes depend on several factors like pressure, temperature and the amount of hydrogen absorbed by the alloy (filling ratio α). The equation (5) shows the model of rate equation to obtain the adjusted formula [6-9].

$$r = \frac{d\alpha}{dt} = k \cdot f(P) \cdot h(\alpha) \tag{5}$$

Where k is:

$$k = A \cdot e^{\left(\frac{-E_a}{R \cdot T}\right)} \tag{6}$$

Therefore two functions have to be determined to obtain the optimal model, f (P) and h (α).

Once the model is determined, the hydrogen flows and the heat fluxes can be predicted through the equations (4) and (5).

## 4 Heat Exchange

Another factor that has high influence in the design of the tanks is the heat exchange process. As seen, the system temperature is an important variable for the kinetic (equation (6)) and for the thermodynamics of the process. Therefore it requires a thermal management of the system flows.

Thermodynamically, the charging and discharging of metal hydrides are exothermic and endothermic processes respectively. So that heat management is important for the deposits

optimal operation. This requires knowledge of the physical characteristics of the deposit to design an optimized canister.

As a first step to managing the heat exchange is necessary to determine the global heat transfer coefficients of the porous media. Thus the hydrogen storage medium presents different thermal characteristics for the gas phase than for the solid phase.

There are different ways to calculate the parameters of the bed. The effective thermal conductivity of the substrate can be calculated with the equation (7) [10].

$$K_{eff} = K_{H_2}\left(1-\sqrt{1-\Psi}\right)\cdot\frac{1}{\Psi-1+\frac{1}{K_{H_2}}}+\sqrt{1-\Psi}\cdot\left[\varphi\cdot K_p + K_{pgp}\cdot(1-\varphi)\right] \quad (7)$$

Where $K_{H_2}$ is the thermal conductivity of hydrogen, $\Psi$ is the porosity factor, $\varphi$ contact materials factor, $K_p$ is the thermal conductivity of the particles, $K_{pgp}$ factor is the thermal conductivity of the particle gas particle interface.

Although there are less accuracy equations that allow obtaining values more quickly and simpler, one example of this equation is the equation (8). These equations do not take into account the contact factors and consider the porous medium as a homogeneous system of two components, the gas phase and solid phase [11].

$$\lambda_e = \varepsilon\lambda_g + (1-\varepsilon)\lambda_s \quad (8)$$

The systems have thermal conductivity values around 1W·m $^{-1}$·K$^{-1}$.For these reason it is necessary to increase the heat transfer capabilities, there is some know solutions for this problem. For example copper fins and metal sponges, increase the values of the bed thermal conductivity up to 2 - 9W·m$^{-1}$·K$^{-1}$.

The use of these systems improves the thermal conductivity of the system and thereby improves the performance of the reservoirs. But those thermal systems add to the canister dense material that does not store hydrogen, thus it decrease the energy density; volumetric and gravimetric.

After determining the global heat transfer from the bed, it is necessary to determine the heat transfer coefficients of the whole system. For this proposal it is necessary to know the geometry of the system to use the proper equations.

In the case of a cylindrical metal hydride tank the global coefficient of heat transfer is expressed by the equation (9) [12].

$$\frac{1}{h_{global}\cdot A} = \frac{1}{h_{medium}A_e} + \frac{\ln\left(\frac{D_e}{D_i}\right)}{2\pi L\lambda_c} + \frac{e_s}{\lambda_s A_i} \quad (9)$$

Where $h_{global}$ is the global heat transfer coefficient of the system, $A$ the contact surface area, $h_{medium}$ the coefficient for the external medium (usually water or air), $A_e$ outer area of the tube contacts, and $D_e$, $D_i$ of the outer and inner diameters of the tubes respectively, $L$ total length of the tube, $\lambda_c$ heat transfer coefficient of tube material and $e_s$ thickness of the storage layer . So the determination of the total value requires knowledge of all materials involved in heat exchanges.

To facilitate the exchange of heat is common to use heat exchange systems such as the ones shown in Figure 3, where the usual heat exchanger fluid is water.


**Figure 3: Heat exchange systems. Left: external Shirt. Centre: internal coil. Right: external envelope for various segments.**

## 5 Size

Size of the metal hydride storage is the first parameter to design a canister. It represents the amount of hydrogen stored, limiting dimension and capabilities to employ a heat exchanger. For example, a canister which takes up all the space of a device could useful, or a system which needs a 5lpm and the design only give 4lpm. It is necessary to fix a several parameters, how capacities, to start a design of a deposit.

## 6 Materials

Polymers, alloys, metals, gases and thermal fluids can be part of a canister. It is important to know all the compatibilities.

Currently, stainless steel, aluminium, hydrogen, several alloys and different polymers conforms typical hydrogen canister. However, in a novel system, with novel materials, it is necessary to check compatibilities.

Materials employed in containment structures need to be stable with other materials in contact. Containment structures are in contact with air and thermal fluid, like other systems.

But with these systems appears news materials in contact, such as hydrogen and the proper metal hydride. It needs to be analysed to avoid accidents. In a first term, working with hydrogen can appears permeation, embrittlement, or another reaction that promote hydrogen leak and a loss of security.

Materials, such as austenitic stainless steel, copper, gold, nickel and aluminium, present lower permeation than others, such as carbon steels. This a property related to crystal lattice,

systems with low permeation have face-centered cubic structure (FCC) because this structure is more resistant to embrittlement. It means that these materials can be used to contain hydrogen gas [13,14]. And the polymers can be a novel material possibility to construct metal hydride storage like high pressure canisters.

Another material in contact is the metal hydride or its metal or alloy. If there are two or more metals in contact it can appear redox reactions. It is important to study the redox potentials before putting in contact metal hydride and canister. This redox reaction can create a region which can be fracturated by action of hydrogen gas, which is a serious risk.

## 7 Conclusions

To design a container there are parameters which are important to take into account.

One of the first parameter is the dimension available or the hydrogen storage. These parameters allow to get a first idea of the system characteristics.

The selection of the proper metal hydride influence on several aspects like kinetics and thermodynamics. With enthalpy and a proper kinetic model, the hydrogen and heat flow can be calculated.

It is important to note that the system has a porosity which gives properties like heat transfer coefficient, and it gives special characteristics to the hydrogen flow. To calculate the global heat transfer coefficient it is important to know the porosity, the materials involved and the geometry to select a proper equation.

And a last term, the materials employed to design the container are important in terms of security and get an optimal design.

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