Heat and mass transfer crisis in a metal hydride accumulator

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Abstract. Heat transfer is the bottleneck in design of efficient metal hydride devices. We have experimentally demonstrated heat and mass transfer crisis at hydrogen absorption in a metal hydride reactor filled with 4.69 kg of Mm₀.₈La₀.₂Ni₄.₁Fe₀.₈Al₀.₁. The crisis results in overheating of the MH bed and considerable slowing of absorption rate. For the case of constant hydrogen flow we have derived a simple solution for energy balance inside the reactor, which predicts the crisis.

1. Introduction

Metal hydrides are used for hydrogen storage, hydrogen purification and hydrogen compression. Some intermetallic compounds absorb hydrogen at near ambient temperatures and pressures, providing advantage over hydrogen storage in compressed or liquefied form in energy efficiency, functionality and safety, especially for applications in distributed and autonomous power.

Heat transfer is the major limiting factor and the methodology for an optimal design of metal hydride devices is still evolving, and a unified design philosophy is lacking [1]. Most of successful studies were at laboratory prototype scale levels and scale up is needed to reach a commercial market [2]. The most successful systems are those that combine a system as simple as possible with the achievement of a target that could not be reached using other alternatives [3].

Metal hydrides are generally used in a form of powdered beds with low effective thermal conductivity ca. 0.1 - 1 W/m K [4]. Equilibrium pressure of the hydrogenation reaction exponentially depends on temperature by the Van't Hoff equation:

\[ p_a(T) = \exp\left(\frac{\Delta S_{MH}}{R} - \frac{\Delta H_{MH}}{RT}\right), \]  

(1)

where \( \Delta H_{MH} \) is the reaction enthalpy and \( \Delta S_{MH} \) is the reaction entropy. Combination of these two factors causes a heat and mass transfer crisis [5-7], which results in a sudden and drop of the reaction rate. As the result it is hard to predict behavior of metal hydride devices even with sophisticated numerical models.

Nevertheless, for some cases analytical solutions are possible, and the most significant is the case of the constant reaction rate [8], for which it is possible to simplify a mathematical model to an ordinary differential equation, and to introduce lumped parameter models [9].

We present experimental results on heat and mass transfer in a metal hydride reactor filled with AB₅ type alloy and demonstrate critical behavior during hydrogen absorption. Hydrogen absorption at sub-critical regime (with constant flow of hydrogen) was modelled by a simple lumped mathematical model.
2. Experiment

Hydrogen absorption was investigated with the help of RSP-1 reactor (Figure 1a). The reactor consists of 4 metal hydride modules with permeable walls, which are installed into a cartridge inside a cylindrical rigid hermetic case with a liquid heat exchanger of area \( A = 0.126 \, \text{m}^2 \) at outer surface. RSP-1 is filled with \( m_{\text{MH}} = 4.69 \, \text{kg} \) of \( \text{Mm}_{0.8}\text{La}_{0.2}\text{Ni}_{4.1}\text{Fe}_{0.8}\text{Al}_{0.1} \) alloy. Maximum capacity of the alloy is \( C_{\text{max}} = 1.35 \, \%\text{wt}., \) \( \Delta H_{\text{MH}} = 35/5 \, \text{kJ/mole H}_2, \) \( \Delta S_{\text{MH}} = 116 \, \text{J/mole H}_2 \text{ K}, \) hysteresis \( \ln(p_{\text{abs}}/p_{\text{des}}) = 0.2, \) heat capacity \( C_p^{\text{MH}} = 420 \, \text{J/kg K}, \) dependence of the equilibrium desorption pressure on temperature is presented in Figure 1b. Desorption isotherm (Figure 1c) can be fitted as:

\[
\frac{C}{C_{\text{max}}} = 0.482 \left( \frac{p}{p_{\text{cl}}(T)} \right)^{1/1.23} + 0.525 \frac{1.74(p/p_{\text{cl}}(T))^{1/0.481}}{1 + 1.74(p/p_{\text{cl}}(T))^{1/0.481}},
\]

Nominal hydrogen capacity of the reactor is 575 stL, i.e. \( C_{\text{nom}} = 1.1 \, \%\text{wt}., \) and nominal charge/discharge rate is \( 1C = 9.6 \, \text{stL/min}. \)

Figure 1. a) Metal hydride reactor RSP-1: 1 – case; 2 – MH module; 3 – MH bed; 4 – liquid heat exchanger; 5 – cover; 6 – gas inlet; 7 heat exchanger cover; 8 – channels for coolant; 9 – gas permeable walls of the MH module; 10 – free volume; 11 – cartridge for MH modules, T1-T3 – thermal sensors; b) equilibrium pressure for the \( \text{Mm}_{0.8}\text{La}_{0.2}\text{Ni}_{4.1}\text{Fe}_{0.8}\text{Al}_{0.1} \) alloy by (1); c) Langmuir-like fit for the desorption isotherm (2) and experimental points.

The reactor is installed in an experimental test bench and provided with connection to a gas supply (hydrogen, nitrogen), a hot and cold water supply (from 10 to 95°C and from 0.05 to 0.3 kg/s), a vacuum system and an automatic control system. Before each experiment the reactor is fully discharged and evacuated. During experiments the reactor is charged with pure hydrogen at inlet pressure 8 bar from a standard 40 L gas cylinder. The gas flow at the inlet/outlet valve of the reactor is controlled and measured.
by a Bronkhorst EL-FLOW Select mass flow meter/controller F-202AC-RAA-55-V, the pressure inside the reactor and the gas supply is measured by Aplisens pressure transmitters model PC28, the water temperature is measured by thin film platinum sensors Heraeus M422, 1 kΩ. The experiments was controlled using LabView software, discretization 1 Hz.

3. Experimental results

The reactor was charged with pure hydrogen at constant flow rates up to 25°C (240 stL/min) with a step 2.5°C (24 stL/min). Hydrogen flow and pressures for two regimes (2.5°C and 5°C) are presented in Figure 2. There are two operational modes for the reactor: subcritical mode with constant flow rate and fast growing pressure and supercritical mode with rapidly declining hydrogen flow rate and stable pressure. The moment of crisis corresponds to the pressure curve knee, pressure inside the reactor becomes close to the inlet pressure and reaction considerably slows down. With the increase of inlet flow rate the crisis occurs earlier and a less hydrogen is charged in the subcritical mode (Figure 3a). Only in the 2.5°C regime the reactor can be charged to nominal capacity ($\text{SoC} = \frac{C}{C_{\text{nom}}}$) without crisis, i.e. with the constant flow rate. As it can be seen from Figure 3b only for the 2.5°C regime the MH bed is not heated up to the maximum temperature. All the curves for pressure and temperature are quite uniform, thus they can be described by similar equations.

![Figure 2](image.png)

**Figure 2.** Hydrogen flow and pressure inside the reactor for two regimes 2.5°C (left) and 5°C (right).

![Figure 3](image.png)

**Figure 3.** a) SoC for different charging regimes; b) temperature inside the MH bed (T2 sensor in Figure 1a).
4. Analytical model
For a constant reaction rate, which corresponds to a constant hydrogen flow and uniform distribution of temperature and pressure inside a metal hydride reactor, it is possible to derive an equation for heat balance in the form of ordinary differential equation. A lumped parameter model of hydrogen absorption is presented in Figure 1. The main assumption:

- Hydrogen is supplied at pressure $p_0$ with constant flow rate $q$;
- the reaction heat is $Q_{MH} = q\Delta H$;
- Pressure and temperature inside the reactor are uniform;
- MH bed cooled by a heat exchanger with area $A$, and the overall heat transfer coefficient $\alpha$ is determined by heat transfer from the metal hydride bed to the wall, heat removed by the heat exchanger is $Q_{HEX} = \alpha A (T - T_0)$;
- For simplicity we assume that the coolant flow rate is high enough to neglect the increase of temperature of coolant, $T_0^{in} = T_0^{out} = T_0$;
- Properties of metal hydride are constant during the process;
- The ratio of the thermal masses of the reactor and the metal hydride bed $B$ represents thermal mass of the reactor.

Thus, the energy equation is:

$$C_p^{MH} m_{MH} (1 + B) \frac{dT}{dt} = q\Delta H - \alpha A (T - T_0)$$  \(3\)

With the following solution for the constant flow rate:

$$T - T_0 = \frac{q\Delta H}{\alpha A} \left(1 - \exp\left[-\frac{\alpha A}{C_p^{MH} m_{MH} (1 + B)} t\right]\right)$$  \(4\)

The same solution could be applied for desorption, given that for the desorption $q<0$, and the reactor temperature decreases. In addition the solution could be generalized for other cases, e.g. changing temperature of heat exchanger, etc.

Comparison of calculated temperature by (3) with experiment is presented in Figure 5 for the regime 2.5C. Indeed, temperature inside the MH bed is far from uniform, since the hydride layer in the MH modules is quite thick and cooled only from one side, moreover the MH modules do not have tight connection to the reactor wall. Nevertheless, there is a good correspondence with mean temperature $(T_2+T_3)/2$ and calculation for $\alpha = 120$ W/m$^2$K, which was determined for the RSP-1 experimentally [10], and close to results for water cooled reactor in [11].
Figure 5. Comparison of calculations by the analytical model with the experiment for 2.5°C.

- a) temperature for several heat transfer coefficients and experimental data for sensors T2 and T3 (see Figure 1);
- b) pressure calculated from temperature with the use of only van’t Hoff equation (1) and with the use of real form of pressure-composition isotherm (2).

Pressure inside the reactor was calculated from temperature, obtained by (3), with the use of van’t Hoff equation (1) and desorption isotherm (2) multiplied by the value of hysteresis. As it can be seen from Figure 5b, van’t Hoff equation is insufficient for prediction of pressure inside the reactor. Pressure curve calculated only by (1) has different form and shows no critical behavior. By taking into account the real shape of pressure-composition isotherm (2) the qualitative agreement with the experiment is reached. Exact agreement cannot be reached, since the temperature inside the reactor is not uniform, contrary to our assumptions. Nevertheless, the condition for crisis is $p_0 = p = 8$ bar, and our model predicts the moment of crisis quite well: 22 min from calculations and 24 in from experiment. Thus, the model can be used as the simple tool for prediction of behavior of metal hydride reactors in subcritical regimes.

5. Conclusions
We have experimentally demonstrated heat and mass transfer crisis at hydrogen absorption in the metal hydride reactor filled with 4.69 kg of $Mn_{0.8}La_{0.2}Ni_{4.1}Fe_{0.8}Al_{0.1}$. The crisis results in overheating of the MH bed and considerable slowing of absorption rate. For the case of constant hydrogen flow we have derived a simple solution for energy balance inside the reactor, which predicts the crisis.

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