Heat and mass transfer crisis in a metal hydride reactor

D O Dunikov$^{1,2}$, V I Borzenko$^1$ and D V Blinov$^{1,2}$

$^1$Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 bld. 2, Moscow, 125412 Russia
$^2$National Research University "Moscow Power Engineering Institute", Krasnokazarmennaya 14, Moscow, 111250 Russia

E-mail: ddo@mail.ru

Abstract. We present a simple lumped mathematical model of hydrogen absorption in a metal hydride reactor with a constant flow rate (sub-critical regime) and use it to predict a heat and mass transfer crisis in the reactor. To verify the model we compare calculations with the experiment on hydrogen absorption in the reactor filled with 5 kg of LaNi$_{4.8}$Mn$_{0.3}$Fe$_{0.1}$ alloy with a hydrogen flow rate of 60 stL/min. The analytical model predicts the heat and mass transfer crisis with good precision.

1. Introduction

Metal hydrides are generally preferred for hydrogen storage applications in distributed and autonomous power due to an advantage over hydrogen compression and liquefaction in energy efficiency, safety, and operational simplicity. Hydrogenation of intermetallic compounds occurs at near ambient temperatures and pressures, thus decreasing losses of useful energy and ensuring an increase of safety.

The methodology for the optimal design of metal hydride devices is still evolving, while unified design philosophy is lacking [1]. Numerous successful studies have been carried out at laboratory prototype scale levels, while scale-up studies are needed to bring metal hydride applications into the commercial market [2]. The consensus is that heat transfer is the major limiting factor, by our estimations almost 60% of articles published in 2017–2019 deal with the heat transfer enhancement. The review by Afzal et al. [1] concludes that the thermal conductivity of metal hydride beds is the major bottleneck for the performance of metal hydride devices, therefore improvement of only thermal conductivity or heat transfer coefficient, or area may not be able to solve the heat transfer bottleneck. 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].

Previously we have demonstrated that a combination of the exponential dependence of hydrogenation equilibrium pressure on temperature and the low thermal conductivity of metal hydride beds leads to significant temperature gradients and non-uniform distribution of hydrogen over a metal hydride bed, which lead to a heat and mass transfer crisis [4–6]. As a result, it is hard to predict the behavior of metal hydride devices even with sophisticated numerical models.

On the other hand, there are some cases, for which analytical solutions are possible. Simplification of the model can be made considering constant hydrogen flow in the inlet and outlet streams [7] and by the introduction of lumped parameter models [8].

In the present paper, we present a simple lumped mathematical model of hydrogen absorption in a metal hydride reactor with a constant flow rate (sub-critical regime) and use it to predict a heat and mass...
transfer crisis in the reactor. To verify the model we compare results with experimental data on hydrogen absorption.

2. Analytical model
A scheme of hydrogen absorption in a metal hydride reactor is presented in Figure 1. Hydrogen at pressure $p_0$ is supplied from a line and a flow regulator maintains a constant mass flow rate $q_{\text{max}}$. The reactor consists of a metal hydride bed and a heat exchanger. We use the following assumptions to create a lumped parameter model:
- Both hydrogen flow $q$ and the reaction rate are constant, thus reaction heat is $Q_{\text{MH}} = q\Delta H$, where $\Delta H$ is hydrogenation enthalpy;
- Pressure and temperature inside the reactor are considered uniform. It is the strongest assumption in our analysis since experiments show that significant temperature gradients exist in metal hydride beds during absorption. The assumption could be fulfilled only for reactors with thin layers of metal hydride and intense liquid cooling;
- Heat transfer from the reactor wall to the coolant in the heat exchanger with the area $A$ is very intense, and the overall heat transfer coefficient $\alpha$ is determined by heat transfer from the metal hydride bed to the wall. Besides, we assume that a coolant flow rate is high enough to neglect the increase of temperature of the coolant, $T_0^{\text{in}} = T_0^{\text{out}} = T_0$;
- Properties of a metal hydride, such as heat capacity $C_{p}^{\text{MH}}$, and the mass of the bed $m_{\text{MH}}$ are constant during the process, and do not depend on hydrogen concentration in the bed;
- The thermal mass of the reactor is represented by the coefficient $B$, which is the ratio of the thermal masses of the reactor and the metal hydride bed.

\[
C_{p}^{\text{MH}} m_{\text{MH}} (1 + B) \frac{dT}{dt} = q\Delta H - \alpha A (T - T_0) \quad (1)
\]

Solution for the constant flow rate is

\[
T - T_0 = \frac{q\Delta H}{\alpha A} \left( 1 - \exp \left[ - \frac{\alpha A}{C_{p}^{\text{MH}} m_{\text{MH}} (1 + B)} t \right] \right) \quad (2)
\]

3. Experiment
Experiments on hydrogen absorption were performed using an RSP-3 reactor (Figure 2). The experimental procedure was similar to our previous investigations [5]. The reactor consists of seven
water-cooled cartridges, with a reaction chamber in a space between Ø18x1 and Ø40x1 mm steel tubes. The reactor is filled with 5 kg of LaNi4.8Mn0.3Fe0.1 alloy, the reactor capacity is 750 stL H2. Heat transfer area is \( A = 0.337 \text{ m}^2 \). Equilibrium pressure depends on temperature by the Van't Hoff equation:

\[
p_s(T) = \exp \left( \frac{\Delta S}{R} - \frac{\Delta H}{RT} \right)
\]

where desorption enthalpy is \( \Delta H = 34.4 \text{ kJ/mole H}_2 \), desorption entropy \( \Delta S = 110 \text{ J/K mole H}_2 \). Maximum capacity of the alloy is \( C_{\text{max}} = 1.35\% \text{wt.} \), hysteresis \( \ln(p_{\text{abs}}/p_{\text{des}}) = 0.13 \), heat capacity \( C_{\text{p, MH}} = 420 \text{ J/kg K} \). Desorption isotherm describes dependence of equilibrium pressure on hydrogen concentration:

\[
\frac{C}{C_{\text{max}}} = 0.849 \frac{0.810(p / p_s(C))^{10.201}}{1 + 0.810(p / p_s(C))^{10.201}} + 0.150 \frac{0.276(p / p_s(C))^{1/1.38}}{1 + 0.276(p / p_s(C))^{1/1.38}}
\]

The RSP-3 reactor was installed in an experimental test bench 12-04 JIHT RAS and provided with a 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 was fully discharged and evacuated. During experiments, the reactor was charged with pure hydrogen from a standard 40 L gas cylinder. The gas flow at the inlet/outlet valve of the reactor was 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 was measured by Aplisens pressure transmitters model PC28, the water temperature was measured by thin-film platinum sensors Heraeus M422, 1 kΩ. The experiments were controlled using LabView software, discretization 1 Hz.

4. Results and discussion
Calculation and experimental results for hydrogen absorption in the RSP-3 at the constant flow \( q_{\text{max}} = 60 \text{ stL/min} \) and the inlet pressure \( p_0 = 0.6 \text{ MPa} \) are presented in Figures 3 and 4. Coolant temperature of \( T_0 = 17.5 \pm 0.5 \text{°C} \) was almost constant during the experiment. The balance mass coefficient was \( B = 1 \). The main uncertainty in the calculations is associated with the heat transfer coefficient. For a liquid-cooled reactor of different design RSP-1 we have experimentally estimated \( \alpha = 120 \text{ W/m}^2 \text{ K} [9] \), which is in good agreement with [10] (113 W/m² K for the reactor cooled with circulating water). The value of \( \alpha \) indeed, greatly depends on the reactor design, thus we've made calculations within the range from 120 to 200 W/m² K.

The hydrogen flow and absorbed volume of hydrogen are presented in Figure 3a. The constant flow rate of 60 stL/min is maintained for 11 min, and 665 stL of hydrogen are absorbed (state of charge 89%). The crisis results in the sharp drop of hydrogen flow rate and for the rest 11 min only 103 stL are charged.
for a total of 770 stL (SOC 103%) in 22 min. Calculations by Eq. (2) show that temperature inside the reactor rises at the beginning of the process to the maximum value, which greatly depends on the value of the heat transfer coefficient. Unfortunately, the RSP-3 reactor doesn't have a temperature sensor inside the metal hydride bed, and there's no possibility to compare calculated temperature with that obtained directly from the experiment.

Nevertheless, the comparison could be made for pressure. Temperatures calculated by Eq. (2) are used for calculation of equilibrium pressure $p_s(T)$ by the Van't Hoff equation (3) multiplied by the value of hysteresis between absorption and desorption. Figure 4a shows that the Van't Hoff equation is insufficient to obtain agreement with the experiment. The calculated pressures are much lower than the experimental values and do not show critical behavior.

To reach the agreement, it is necessary to take into account the dependence of equilibrium pressure on hydrogen concentration in the alloy, described by Eq. (4). Hydrogen concentration $C$ is calculated from the value of absorbed hydrogen calculated as $q_{\text{max}}$, and the mass of the metal hydride bed. Then the value of pressure at isotherm $p_s(C)$ was obtained from Eq. (4) and the final value of pressure was calculated as $p = p_s(C) p_s(C)$.

Figure 4b shows that the good agreement between the calculation and experiment is reached using the real form of pressure-composition isotherm. The crisis occurs when the pressure inside the reactor becomes close to the pressure in the supply line. At this moment there is no pressure difference, and the gas flow stops. In this case, the pressure shows critical behavior with a sharp rise at the moment of crisis, and during the crisis, the calculated pressures become higher than the pressure in the supply line. After this moment the analytical model does not work since it presumes the constant hydrogen flow rate at the reactor inlet.

Moreover, the good agreement is reached for the heat transfer coefficient $\alpha = 150$ W/m$^2$K. The quantitative agreement between our simple model and experiment is reached because the metal hydride layer in the RSP-3 reactor is thin (<10 mm) and intensively cooled, thus the condition of the uniform temperature inside the bed is fulfilled. In thicker layers of a metal hydride, temperature obviously would be non-uniform and our model would not give precise quantitative predictions. Nevertheless, the proposed model can be used as a simple tool to predict a crisis in metal hydride devices without complicated numerical simulation.

Figure 3. Flow rate and charged volume of hydrogen (a) during the experiment and calculated temperatures (b).
Figure 4. Comparison of experimental results with calculations. Solid lines: pressure in the supply line $p_0$ and inside the reactor during the experiment; dashed lines: (a) calculation of pressure with the use of Van't Hoff equation (3) and (b) Van't Hoff equation (3) including dependence on hydrogen concentration by equation (4).

Conclusion
Under certain conditions (constant hydrogen flow, uniform temperature, and sufficient cooling) heat transfer in a metal hydride reactor can be calculated by simple lumped mathematical models. We have obtained an analytical solution for the evolution of temperature in the metal hydride reactor for the sub-critical regime of charge at constant hydrogen flow. The crisis occurs when the pressure inside the reactor becomes close to the supply pressure, and the reaction stops as pressure difference vanishes. Comparison with the experiment on absorption in the metal hydride reactor filled with 5 kg of LaNi$_{4.8}$Mn$_{0.3}$Fe$_{0.1}$ alloy has shown the good agreement both for the occurrence of crisis and pressure evolution in the reactor.

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References
[1] Afzal M, Mane R and Sharma P 2017 Int. J. Hydrogen Energ. 42 30661–82
[2] Muthukumar P, Kumar A, Raju N N, Malleswararao K and Rahman M M 2018 Int. J. Hydrogen Energ. 43 17753–79
[3] Bellosta von Colbe J et al. 2019 Int. J. Hydrogen Energ. 44 7780-808
[4] Borzenko V, Dunikov D and Malyschenko S 2011 High Temperature 49 249-56
[5] Blinov D V, Borzenko V I, Dunikov D O and Romanov I A 2014 Int. J. Hydrogen Energ. 39 19361–8
[6] Borzenko V I, Blinov D V, Dunikov D O and Leontiev A I 2018 J. Phys. Conf. Ser. 1128 012126
[7] Talagañis B A, Meyer G O and Aguirre P A 2011 Int. J. Hydrogen Energ. 36 13621–31
[8] Xiao J, Tong L, Bénard P and Chahine R 2020 Energy 191 116535
[9] Borzenko V, Dunikov D and Malyschenko S 2008 Proc. of 17th World Hydrogen Energy Conference (WHEC 2008) (Australia: Brisben)
[10] Kaplan Y 2009 Int. J. Hydrogen Energ. 34 2288–94