Heat and mass transfer in a metal hydride reactor: combining experiments and mathematical modelling

D O Dunikov¹,², V I Borzenko¹, D V Blinov¹,², A N Kazakov¹, I A Romanov¹ and A I Leontiev¹

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

E-mail: ddo@mail.ru

Abstract. Heat transfer in porous metal hydride (MH) beds determines efficiency of MH devices. We present a COMSOL Multiphysics numerical model and experimental investigation of heat and mass transfer in a MH reactor filled with 4.69 kg of AB5 type alloy (Mm₀.₈La₀.₂Ni₄.₁Fe₀.₈Al₀.₁). To achieve an agreement between the model and experiments it is necessary to include a flow control device (inlet valve or flow regulator) into the model. We propose a simplified and easy-to-calculate boundary condition based on a porous domain with variable permeability at reactor inlet. The permeability of the domain is connected with hydrogen mass flow by a PID controller. Thus, boundary conditions for the inlet pressure and mass flow are coupled and heat transfer inside the reactor could be calculated without additional assumptions applied to heat and mass transfer in the MH bed.

1. Introduction
Metal hydrides are used for hydrogen storage, purification, compression and for other applications. Their advantage is the property of selective hydrogen absorption at near ambient temperatures and pressures, which leads to energy efficiency, functionality and safety, especially for applications in distributed and autonomous power.

Many attempts have been made to identify the relationship between operating and design variables and the performance of metal hydride devices, and numerous models have been presented [1]. Unfortunately, a lot of previous works are based on very strict and unnatural assumptions, rarely verified by experiments. Since the heat transfer inside a metal hydride bed is the bottleneck for the performance [2], the efforts in model development are mostly concentrated in more detailed description of the MH bed. Nevertheless, heat generation is directly coupled with mass transfer, and experiments show that flow controllers at hydrogen inlet and outlet could have a significant influence on the results [3]. Recent investigations show that control-oriented models are needed for system design [4].

We present a mathematical model for the processes in a MH reactor implemented in COMSOL Multiphysics and compare simulation results with experiments. Our goal is to show a necessity to include a hydrogen supply and control devices into the model to reach an agreement with experiments.
2. Mathematical model

Our mathematical model is based on the model developed by the MPEI group led by G.G. Yankov in cooperation with the JIHT RAS group, including authors of the present paper [5–7]. We have implemented the model in COMSOL Multiphysics with the help of D.O. Lazarev (COMSOL).

A metal hydride reactor consists of several domains, including a porous metal hydride bed with a solid matrix from AB5 type alloy and hydrogen as a fluid, and free space filled with hydrogen and solid walls of the reactor made of structural steel. Properties of hydrogen and steel are taken from the COMSOL library. The model includes the description of gas flow in the free space and pores, hydrogen absorption and desorption by solid particles in the porous metal hydride bed, heat transfer in the free space and porous medium, and solid walls are considered as thin layers.

Gas flow is described by the Navier–Stokes equations in the free space and Brinkman equations in the porous medium. We use the Free and Porous Media Flow (fp) interface, and a mass source is described by equations for the reaction kinetics. Heat transfer is described by the energy equations for gas, porous and solid phases, and the Heat Transfer in Porous Media (ht) is used. Pressure and velocities are taken from the fp interface and heat source is determined by the reaction kinetics. Mass conservation is calculated with the use of the Domain ODEs and DAEs (dode) interface. In the metal hydride bed we define a field variable \( X_{H} \), which represents the fraction of transformed solid phase in the gas-solid chemical reaction [3]:

\[
X_{H} = \frac{C}{C_{\text{max}}}, \quad \frac{dX_{H}}{dt} = X_{\text{rate}}
\]

where \( C_{H} \) is the hydrogen concentration in metal and \( C_{\text{max}} \) is the maximum concentration. The rate of the reaction is determined as:

\[
X_{\text{rate}} = \begin{cases} 
C_a \exp(-E_a / RT) \ln(p / p_{eq}^{\text{abs}})(1 - X_{H}) & \text{if } p > p_{eq}^{\text{abs}}(T, C_{H}) \\
0 & \text{if } p < p_{eq}^{\text{abs}}(T, C_{H}) \\
C_d \exp(-E_d / RT) \ln(p / p_{eq}^{\text{des}})X_{H} & \text{if } p < p_{eq}^{\text{des}}(T, C_{H})
\end{cases}
\]

The equilibrium \( p_{eq} \) pressure of the metal-hydrogen reaction depends both on \( T \) and \( C_{H} \), and could be calculated as a composition of two terms:

\[
p_{eq} = p_s(T)\tilde{P}(C_{H}); \quad p_s(T) = \exp(\Delta S_{MH} / R - \Delta H_{MH} / RT)
\]

where \( \tilde{P} \) is the dimensionless pressure-composition isotherm and \( p_s \) is the plateau pressure calculated by the van’t Hoff equation, \( \Delta H_{MH} \) and \( \Delta S_{MH} \) are the desorption enthalpy and entropy. For the Mn_{0.8}La_{0.2}Ni_{4.1}Fe_{0.8}Al_{0.1} alloy the dimensionless pressure-composition isotherm is fitted as:

\[
\frac{C_{H}}{C_{\text{max}}} = 0.482 \frac{0.656\tilde{P}^{1/1.23}}{1 + 0.656\tilde{P}^{1/1.23}} + 0.525 \frac{1.74\tilde{P}^{1/0.481}}{1 + 1.74\tilde{P}^{1/0.481}}
\]

Hysteresis between absorption and desorption is defined by a constant:

\[
C_{\text{hyst}} = \ln(p_{eq}^{\text{abs}} / p_{eq}^{\text{des}})
\]

Mass and heat sources are calculated in MH domains as:

\[
Q_{m} = -(1 - \varepsilon)\rho_{s} C_{\text{max}} X_{\text{rate}}; \quad Q_{H} = -Q_{m} \Delta H_{MH} / M_{H_2}
\]

where \( \varepsilon \) is the MH bed porosity and \( M_{H_2} \) is the molecular mass of hydrogen.

The MH bed permeability and effective thermal conductivity are calculated as:
\[ \kappa = d_p^2 \left( \frac{e}{1-e} \right)^2 / 180; \quad k_{\text{eff}} = k_H / e^3 \]  

(7)

where \( d_p \) is the mean diameter of MH particles. Due to the small size of the particles the thermal conductivity of the solid matrix \( k_s \) is much less than \( k_{\text{eff}} \).

Initial conditions include initial hydrogen concentration \( C_H^0 = C_{\text{max}} X_H^0 \), zero velocities, constant temperature \( T_0 \) and constant pressure \( p_0 = P_{\text{eq}}^{\text{abs}}(T_0, C_H^0) \). Boundary conditions include convective heat flux at steel walls \( q_0 = h_{\text{wall}} (T_\text{wall} - T) \), temperature \( T_0 \) at the inlet, and we need the last condition for the gas flow. For metal hydride reactors there could be two types of boundary conditions at the reactor inlet: we can set a mass flow or a pressure (both either constant or by a function) at the boundary. Both have own limitations, as it was shown in our analytical model [8] the condition of constant mass flow leads to uncontrolled temperature and pressure rise. On the other hand, the condition of constant pressure \( p_{\text{in}} \) makes hydrogen flow at the inlet unpredictably high. Thus, both variants are physically incorrect and the choice of the appropriate boundary condition is discussed in section 5.

3. Reactor design and experimental setup

Experiments were performed using the RSP-1 reactor (Figure 1) [8, 9]. The cylindrical reactor with the inner chamber of height \( L_{\text{reactor}} \) and radius \( R_{\text{reactor}} \) includes 4 metal hydride modules with MH layer of height \( L_{\text{MH}} \) and thickness \( h_{\text{MH}} \) each filled with \( m_{\text{MH}} \) of \( \text{Mn}_{0.8}\text{La}_{0.2}\text{Ni}_{4.1}\text{Fe}_{0.8}\text{Al}_{0.1} \) alloy, equally distributed between the modules.

The experiments are similar to [8, 9], at the test bench the reactor is provided with gases (hydrogen, nitrogen) and water (10–95°C, 0.05–0.3 kg/s) and connected to vacuum and automatic control systems. Before each experiment the reactor is fully discharged, evacuated, and then charged with pure hydrogen from a standard 40 L gas cylinder via pressure reducer. The gas flow at the inlet valve of the reactor is controlled and measured by a Bronkhorst EL-FLOW Select mass flow meter/controller F-202AC-RAA-55-V. For the pressure measurement Aplisens transmitters model PC28 is used, and the water temperature is measured by thin film platinum sensors Heraeus M422, 1 kΩ. The experiments are controlled using LabView software, with discretization being 1 Hz.

The reactor dimensions, alloy and thermal properties are presented in Table 1. Nominal hydrogen capacity of the reactor is 575 stL, and nominal charge/discharge rate is 1C = 9.6 stL/min.

4. Experimental results

The reactor was charged with pure hydrogen at constant flow rates of up to 25C (240 stL/min) with a step of 2.5C (24 stL/min). In our previous works [8, 9] we have demonstrated, that 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 crisis occurs when pressure inside the reactor becomes close to the inlet pressure and reaction rate \( X_{\text{rate}} \) Eq. (2) considerably slows down. With the increase of inlet flow rate the crisis occurs earlier and less hydrogen is charged in the subcritical mode; thus only in the 2.5C regime the reactor can be charged to nominal capacity with the constant flow rate.

5. PID mass flow regulation at the reactor inlet

Modelling of the RSP-1 reactor with the constant pressure boundary condition contradicts with the experimental results (Figure 2). The reactor inlet is modelled as the 6mm steel tube and there are no restrictions for hydrogen flow, thus the calculated mass flow is much higher than experimental values. Real metal hydride devices are usually connected to hydrogen sources (cylinders, electrolyzers, etc.) by tubes with valves and other equipment, thus they have limited mass flow capacity and considerable hydraulic resistance and should be considered in the formulation of boundary conditions.
Table 1. Parameters of the model.

| Parameter | Value |
|-----------|-------|
| $\Delta H_{MH}$, kJ/mole | 34.1 |
| $\Delta S_{MH}$, J/mole K | 110 |
| $m_{MH}$, kg | 4.69 |
| $C_{max}$, %wt. | 1.35 |
| $C_{kst}$ | 0.2 |
| $d_p$, mm | 0.01 |
| $\varepsilon$ | 0.56 |
| $\rho_s$, kg/m$^3$ | 8300 |
| $C_p$, J/kg K | 420 |
| $k_i$, W/m K | 0.01 |
| $k_{BH}$, W/m K | 0.183 |
| $m_{BH}$, kg | 4.69 |
| Nominal capacity, stL | 575 |
| 1C flow rate, stL/min | 9.6 |
| $L_{reactor}$, mm | 390 |
| $R_{reactor}$, mm | 50 |
| $L_{BH}$, mm | 69 |
| $h_{BH}$, mm | 18 |
| $h_{ev}$, W/m$^2$ K | 2000 |
| $T_0 = T_{ext}$, °C | 16.5 |
| $p_{in}$, bar | 7.5 |

Figure 1. RSP-1 reactor:
1 – case; 2 – MH module; 3 – MH bed; 4 – liquid heat exchanger; 5 – cover; 6 – gas inlet; 7 heat exchanger cover; 8 – coolant inlet; 9 – MH module permeable walls; 10 – free space; 11 – cartridge, T1-T3 – thermal sensors.

To control the hydrogen flow, we use the Bronkhorst EL-FLOW Select controller. Measurements are based on the bypass principle, part of the gas stream flows through a sensor, and the main part of the stream goes through a laminar flow element, which consists of a stack of stainless steel discs with flow channels, having similar characteristics as the flow sensor. Signals from the sensor are used to operate a control valve, where the flow is controlled by changing a distance between a plunger and an orifice. Indeed, a detailed simulation of the controller is complicated and excessive, thus we model the controller as a 10 mm long porous insert in the Ø6mm inlet tube. The insert is modelled by the fp interface, the solid matrix is the structural steel with porosity of 0.5 and variable permeability. The porous insert creates hydraulic resistance at the inlet and makes the calculations closer to the experiments; the dashed line in Figure 3 corresponds to the porous insert with constant permeability of $10^{-12}$ m$^2$.

Nevertheless, to reach an agreement between the model and the experiments we need a feedback controlled to simulate the real one. We use a PID controller, created by an add-in from the COMSOL Multiphysics Add-in Library. The add-in creates a 0D component that implements the controller:

$$u(t) = u_{bias} + k_p(q_{set} - q(t)) + k_i \int_0^t(q_{set} - q(t)) - k_d \frac{dq(t)}{dt}; \quad \kappa_{ins} = (u(t) + 1) \cdot 10^{-14}$$ (8)
where $q_{set}$ is the mass flow setpoint in stL/min, and the inlet mass flow $q(t)$ is measured as an average over a boundary probe inside the inlet tube, the PID constants $u_{bias}$ and $k_d$ are set to 0, and the proportional $k_p$ and integral $k_i$ gain constants are varied and the controller value is in the range between 0 and $u_{max}$, which correspond to closed and fully open valve.

The results for $q_{set} = 24$ stL/min, $k_p = 5$, $k_i = 1000$ and $u_{max} = 300$ and 3000 are presented in Figure 3 in comparison with the experimental results for 2.5C.

**Figure 2.** Hydrogen mass flow (right) and volume (left) for the regimes from 2.5C to 25C in comparison with results of calculations with different boundary conditions at the inlet.

**Figure 3.** Comparison of the experimental results for 2.5C regime (blue) and the model with PID regulation (red): temperature at the center of the top MH module (top left), pressure (top right), charged volume (bottom left) and hydrogen mass flow at the inlet (bottom right).

The control variables determine the speed of reaction of the controller, while $u_{max}$ determines the maximum flow capacity and has significant influence on the results, restricting evolution of the
pressure and, thus, heat and mass transfer in the MH reactor. With the use of PID controlled we’ve managed to reach good agreement with experiment. Some discrepancy is observed for the temperature of the point probe in the center of the top MH module, which is connected with significant inhomogeneity of temperature field inside the MH bed (Figure 4) and development of a hot core in the center [10], while the real sensor is not a point and averages temperature over a region inside the MH bed. Nevertheless, all the integral characteristics are in the agreement.

**Figure 4.** Temperature and $X_{\text{H}}$ for the top MH module at 900 s.

**Conclusions**

We have developed the mathematical model implemented in COMSOL Multiphysics and compared simulation results with experiments in a metal hydride reactor filled with 4.69 kg of the $\text{Mm}_{0.8}\text{La}_{0.2}\text{Ni}_{4.1}\text{Fe}_{0.8}\text{Al}_{0.1}$. The results show that the agreement between the model and experiments could be reached with the help of the PID controller at the reactor inlet, which simulates the real flow meter/controller and couples boundary conditions for the inlet pressure and mass flow.

**Acknowledgements**

The work was funded by the Russian Science Foundation (project No. 17-19-01738).

**References**

[1] Mohammadshahi S S, Gray E M and Webb C J 2016 *Int. J. Hydrogen Energ.* 41 3470–84
[2] Afzal M, Mane R and Sharma P 2017 *Int. J. Hydrogen Energ.* 42 30661–82
[3] Blinov D V, Borzenko V I, Dunikov D O and Romanov I A 2014 *Int. J. Hydrogen Energ.* 39 19361–8
[4] Keow A L J, Mayhall A, Cescon M and Chen Z 2021 *Int. J. Hydrogen Energ.* 46 837–51
[5] Minko K B, Artemov V I and Yan’kov G G 2014 *Int. J. Heat Mass Trans.* 68 683–92
[6] Artemov V I, Lazarev D O, Yan’kov G G, Borzenko V I, Dunikov D O and Malysheenko S P 2004 *High Temp.*+ 42 987–95
[7] Artemov V I, Borovskikh O V, Lazarev D O, Yankov G G, Borzenko V I and Dunikov D O 2008 *Proc. of 17th World Hydrogen Energy Conference* 628–31
[8] Dunikov D O and Borzenko V I 2020 *J. Phys. Conf. Ser.* 1683 052018
[9] Borzenko V, Dunikov D and Malysheenko S 2011 *High Temp.*+ 49 249–56
[10] Borzenko V I, Blinov D V, Dunikov D O and Leontiev A I 2018 *J. Phys. Conf. Ser.* 1128 012126