Computational Analysis of Metal Hydride Reactor for Thermal Energy Storage

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Introduction

Metal hydride based thermal energy storage systems belong to the category of heat storage systems which rely on reversible thermo-chemical reactions to store and release heat. Specifically, these systems utilize metal/alloy hydride decomposition (endothermic) and formation (exothermic) reactions to store and liberate heat respectively. Hydride forming metals/alloys like Mg, $LaNi_5$, FeTi etc. have long been under research for the purpose of solid state hydrogen storage. Thermal energy storage devices based on many of these materials have received considerable attention in areas like solar thermal systems as they promise high energy storage density (both volumetric and gravimetric) and discharge temperatures. The core components of these systems are reactors enclosing the solid-gas reaction system of metal/alloy and hydrogen. The desired features in design of the reactors include effective hydrogen transport into the porous solid metal/alloy, efficient heat supply to and from the reaction system and structural stability in the operating pressure and temperature range which in case of materials like magnesium may go up to 40 bar and 400°C. Simulation of conceptual designs of reactors aid in design improvements by analysing these requirements, qualitatively and quantitatively, but require handling the chemical reaction, fluid flow and heat transfer simultaneously with appropriate material models.

In the present study, a reactor concept for heat storage, with hydrogen supply under specified pressure conditions and with heat exchanger coils carrying heat transfer fluid is analysed using COMSOL Multiphysics®. The reactor geometry is shown in Figure 1.

Theory

The solid-gas reaction system of metal/alloy and hydrogen is constituted by gaseous hydrogen existing in the void spaces of a porous solid phase in powder or pellet form composed of unreacted metal/alloy and its hydride. These systems may exist in equilibrium or not. In equilibrium, the state of hydrogen gas in the void volume can be completely described by specifying the pressure and temperature. Also, when in equilibrium, the fraction of metal/alloy reacted or converted into hydride can be expressed as a function $x = x(p, T)$ of the gas pressure and local temperature. This characteristic model of a metal/alloy – hydrogen system is conventionally presented as pressure-concentration isotherm. The relevant information with respect to a heat storage system is that increasing pressure or decreasing temperature shifts the equilibrium to a higher value of reacted hydrogen. As the system shifts to a new equilibrium through forward or reverse reaction, heat is released or consumed while consuming or liberating hydrogen.

A system not in equilibrium will have hydrogen formation or decomposition (net reaction) in progress which is described using models for kinetics in which the rate of change of fraction of reacted hydrogen is expressed in terms of its instantaneous value, gas pressure and local temperature.

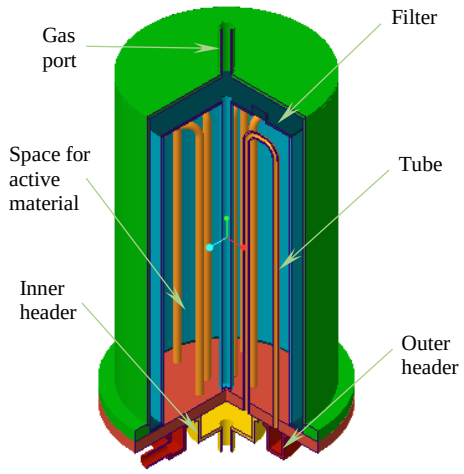

Figure 1. Reactor configuration

Governing equations and simulation methods

In the present study, $LaNi_5$ is used as the active material in the reactor. Their thermophysical property values are listed in Table 1.

Table 1. Thermophysical properties of $LaNi_5$ [1–3]

	$LaNi_5$
Density (kgm^{-3})	7960
Porosity	0.69
Specific heat capacity ($Jkg^{-1}K^{-1}$)	419
Maximum hydrogen fraction ($kgkg^{-1}$)	0.0136
Permeability (m^2)	1×10^{-12}
Thermal conductivity (W/mK)	1.32

A description of equilibrium characteristics is given below [4]. The parameter values are listed in Table 2.

$$\ln\left(\frac{p}{p^{\ominus}}\right) = A - \frac{B}{T} + (\phi \pm \phi_s)\tan\{\pi(x-0.5)\} \pm \frac{\beta}{2}$$

where + is for hydride formation and – is for hydride decomposition.

Table 2. Parameters of equilibrium characteristics of $LaNi_5$ [4]

	$LaNi_5$
$p^{\ominus}$ (Pa)	1×10^5
A	13.44
B (K)	3780
ϕ	0.038
$\tilde{\phi}$	0
β	0.137

The equilibrium characteristics, when expressed as isotherms, exhibit a plateau (pressure p_p) in the concentration-pressure plane. The plateau pressure is related to temperature of isotherm by the van 't Hoff equation. The equation contains enthalpy change during hydrogen formation.

$$\ln\left(\frac{p_p}{p^{\ominus}}\right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

The kinetics model for rate of change of reacted fraction of $LaNi_5$ with time is given below. The parameters are listed in Table 3.

$$\frac{dx}{dt} = \begin{cases} \sigma_f \cdot \exp\left(\frac{-E_f}{RT}\right)\ln\left(\frac{p}{p_{ef}}\right)(1-x), & p > p_{ef} \\ \sigma_d \cdot \exp\left(\frac{-E_d}{RT}\right)\left(\frac{p}{p_{ef}}-1\right)x, & p < p_{ed} \\ 0, & p_{ed} < p < p_{ef} \end{cases}$$

p_{ef} and p_{ed} are obtained from the equilibrium characteristics.

Table 3. Parameters in the reaction kinetics model for $LaNi_5$ [5]

	$LaNi_5$
σ_f (s^{-1})	59.187
E_f ($Jmol^{-1}$)	21170
σ_d (s^{-1})	9.57
E_d ($Jmol^{-1}$)	16450

The geometry is created using built-in tools of COMSOL Multiphysics®. The outer header was disabled to make use of symmetry of the domain. The domain of analysis is shown in Figure 2.

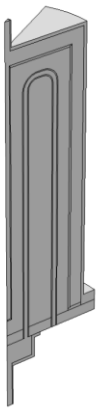

Figure 2. Domain of analysis

The physics models are obtained from the CFD module, heat transfer module and mathematics module. The velocity of gaseous hydrogen outside the active material is neglected for initial simulations. The Darcy's law physics from CFD module solves for the pressure and velocity fields associated with hydrogen flow through the porous bed. The governing equations are:

$$\frac{\partial}{\partial t}(\epsilon\rho) + \nabla\cdot(\rho\boldsymbol{u}) = Q_m$$

$$\boldsymbol{u} = -\frac{\kappa}{\mu}\nabla p$$

Brinkman Equations were initially tried to model the flow resistance through the porous bed, but were replaced by Darcy's model for initial simulations due to issues with convergence.

The material of solid reactor elements is stainless steel and the filter is sintered stainless steel. The properties used are listed in Table 4 and Table 5.

Table 4. Properties of stainless steel

	Stainless steel
Density (kgm^{-3})	7990
Specific heat capacity ($Jkg^{-1}K^{-1}$)	450
Thermal conductivity (W/mK)	15

Table 5. Properties of sintered stainless steel

	Sintered stainless steel
Density (kgm^{-3})	6900
Porosity	0.14
Specific heat capacity ($Jkg^{-1}K^{-1}$)	500
Permeability (m^2)	9×10^{-13}
Thermal conductivity (W/mK)	6.8

Darcy's law is coupled with a Heat Transfer in Porous Media physics from Heat Transfer module which solves for temperature field in the whole reactor domain (solid or fluid phases are added and assigned appropriately to non-porous domains). The governing equations are:

$$\left(\rho C_p\right)_{eff}\frac{\partial T}{\partial t} + \rho C_p \boldsymbol{u}\cdot\nabla T + \nabla.\boldsymbol{q} = Q$$
$$\boldsymbol{q} = -k_{eff}\nabla T$$

The Coefficient Form PDE physics from Mathematics module, is tuned and reduced to the reaction kinetics model of chosen material. The model, depending on gas pressure from Darcy's law and temperature field from Heat Transfer in Porous Media, solves for the field of reacted fraction of hydrogen. The hydrogen and heat absorption or liberation due to reaction of hydrogen with metal/alloy are modelled respectively by adding a mass source term to the Darcy's law and a heat source term to the heat transfer in porous media physics. Both terms are derived from the reduced Coefficient Form PDE physics. The flow of heat transfer fluid inside the tubes is modelled by Laminar/Turbulent Flow physics which is also coupled to the earlier mentioned heat transfer physics.

Simulation results

Results obtained from the time dependent studies on the reactor during hydride formation and decomposition are presented below. During hydrogen absorption, hydrogen gas pressure is maintained at 3bar outside the filter and cooling water is let in through the outer arms of the tubes with an inlet velocity of 0.05m/s and temperature 303K. During decomposition the gas pressure around the bed is set to 1.5bar and the water inlet is set to a temperature of 353K. The distributions of absorbed hydrogen and domain temperature along with heat transfer fluid outlet temperature during hydride formation are shown in Figure 3 to Figure 7.

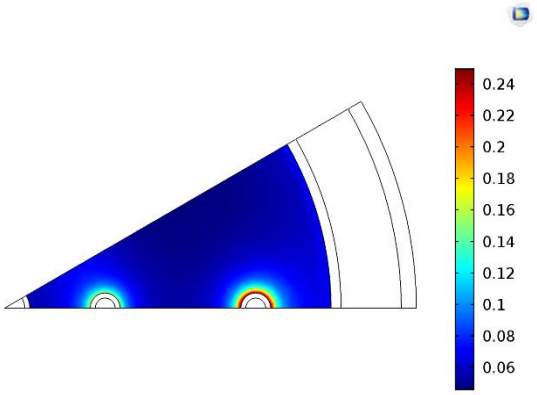

Figure 3. Reacted fraction after 500s under 3bar hydrogen pressure and inlet water temperature at 303K

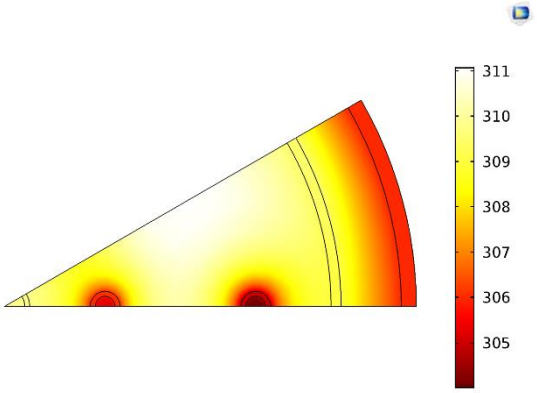

Figure 4. Temperature (in Kelvin) of active material after 500s under 3bar hydrogen pressure and inlet water temperature at 303K

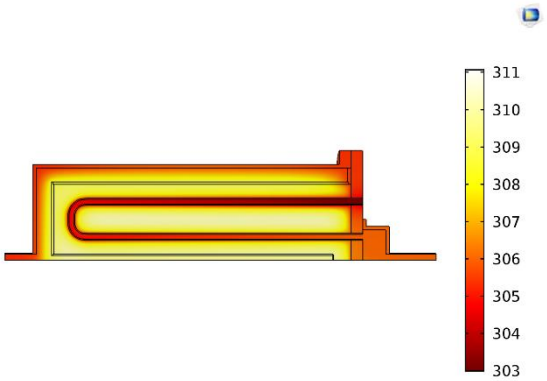

Figure 5. Temperature (in Kelvin) in domain after 500s under 3bar hydrogen pressure and inlet water temperature at 303K

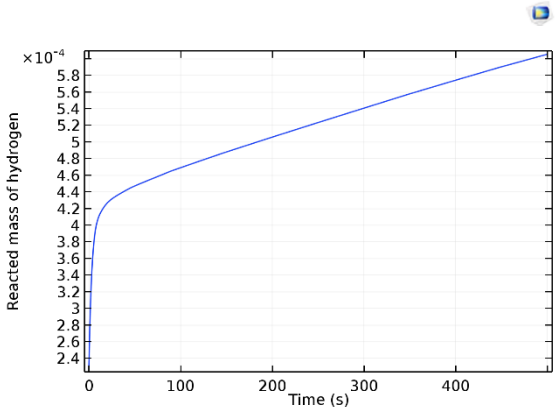

Figure 6. Reacted mass of hydrogen (in kg) with active material under 3bar hydrogen pressure and inlet water temperature at 303K

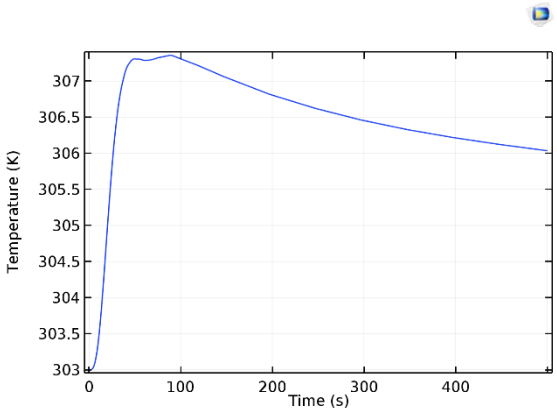

Figure 7. Outlet water temperature with active material under 3bar hydrogen pressure and inlet water temperature at 303K

The reacted mass of hydrogen in Figure 6 shows that the reaction is not complete after 500s. If we are to have a fast heat consuming and releasing reactor, the heat transfer apparatus inside has to be much more effective. The results for decomposition are shown in Figure 8, Figure 9 and Figure 10.

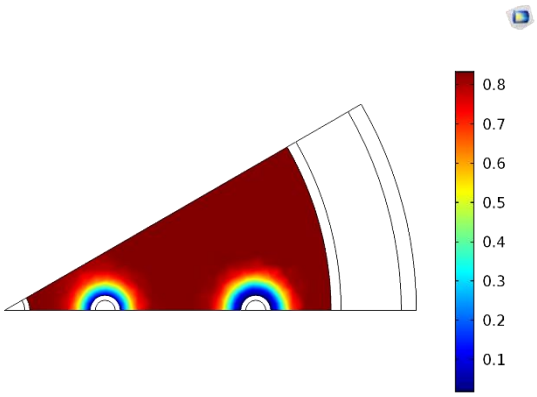

Figure 8. Reacted fraction after 300s under 1.5bar hydrogen pressure and inlet water temperature at 353K

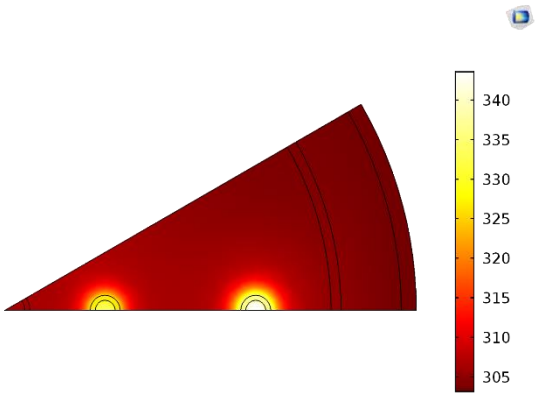

Figure 9. Temperature (in Kelvin) of active material after 300s under 1.5bar hydrogen pressure and inlet water temperature at 353K

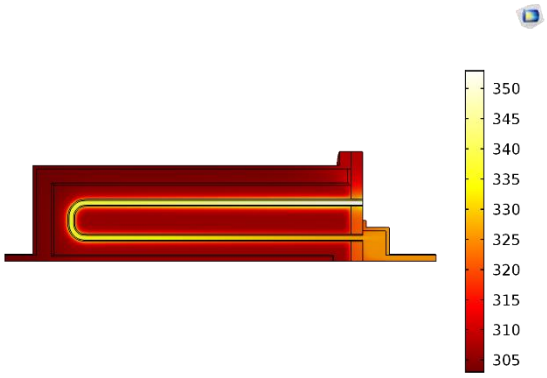

Figure 10. Temperature (in Kelvin) in domain after 300s under 1.5bar hydrogen pressure and inlet water temperature at 353K

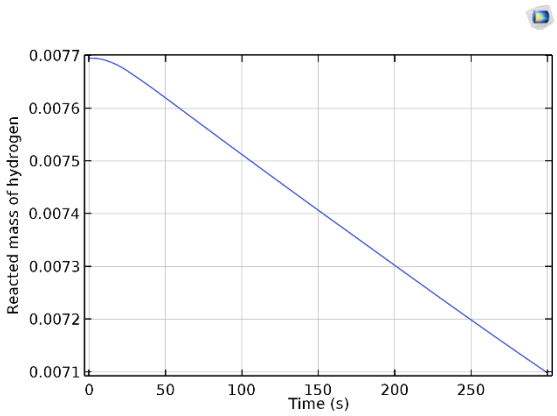

Figure 11. Reacted mass of hydrogen (in kg) with active material under 1.5bar hydrogen pressure and inlet water temperature at 353K

The cross-sectional distribution of reacted fraction of metal can help in determining the maximum tube spacing which ensures completion of reaction within desired heating or cooling time. The cross-sectional temperature distribution can be utilized in developing effective fins for the tubes without short circuiting the hot and cold arms of the bent tubes.

Conclusions

The simulation can be made more robust by utilizing the Chemistry module for handling the metal – hydrogen reaction. The design of the reactor can be improved by optimizing the number of tubes, tube spacing and addition of fins on tubes for enhancing heat transfer.

References

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