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NUMERICAL SIMULATION OF HYDROGEN SORPTION IN METAL HYDRIDE BASED STORAGE BED USING LATTICE BOLTZMANN METHOD

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ABSTRACT

Heat transfer is the major sorption rate controlling factor in the storage of hydrogen in solid state hydrogen storage devices. Lattice Boltzmann Method is an important computational scheme for the heat and mass transfer simulation of intricate systems. The present paper deals with the numerical study of the hydrogenation performance of the LaNi₅ based alloy bed with the LBM based algorithm. Effect of different geometric and operating parameters on the sorption performance of the device is studied.

NOMENCLATURE

| | |
|------------|--|
| c | Specific heat, $\text{J kg}^{-1}\text{K}^{-1}$ |
| D | Diffusivity, $\text{m}^2 \text{s}^{-1}$ |
| e | Microscopic velocity, ms^{-1} |
| E_a | Activation energy, J mol^{-1} |
| f, g | Distribution functions |
| h | Heat transfer coefficient, $\text{W m}^{-2} \text{K}^{-1}$ |
| k | Thermal conductivity, $\text{Wm}^{-1} \text{K}^{-1}$ |
| m | Rate of hydrogen absorbed, $\text{kg m}^{-3} \text{s}^{-1}$ |
| p | Pressure, Pa |
| R | Univ. gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) |
| t | Time, s |
| T | Temperature, K |
| H^0 | Heat of formation, J kg^{-1} |
| ϵ | Porosity |
| ρ | Density |

Subscripts

| | |
|------------|---------------------|
| <i>e</i> | Effective |
| <i>eq</i> | Equilibrium |
| <i>f</i> | Heat transfer fluid |
| <i>i</i> | Direction index |
| <i>s</i> | Solid |
| <i>sat</i> | Saturated |
| <i>w</i> | Weighing factor |
| 0 | Initial value |

1.INTRODUCTION

Metal hydrides are formed on exposure of certain metals or alloys to hydrogen at ordinary temperatures and pressures. Metal hydrides as hydrogen storage media offer various beneficial features such as high volumetric storage capacity, fast reaction kinetics, large number of charge-discharge cycles and safety. Most hydrogen storage materials absorb hydrogen releasing considerable amount of heat to the cooling media, and it is the most important rate limiting step in the storage of hydrogen.

Experimental study of heat and mass transfer in hydrogen storage devices is not always feasible due to several factors which include the availability and cost of materials, reactor geometry, heat transfer augmentation techniques employed, reliable data acquisition methods and other inherent problems associated with experimentation. Numerical simulation of the storage devices hence gains importance. Most heat and mass transfer studies in hydride beds deal with 1D, 2D or 3D formulation of conservation equations in cylindrical coordinates. Several early investigations reported in literature deal with the radial variation of concentration and temperature. Lucas and Richards [1] used 1D general conduction equation with no internal heat generation for the representation of hydride beds. Majority of the work reported on the numerical study of heat and mass transfer in hydride bed deals with 2D conservation equations in differential form. These models fall into two different categories based on the generality. In the simplified form, mass and energy equations are applied for the bed as a homogenized medium. Effect of convection is neglected [2]. In the more generalized version of equation, separate mass and energy equations are developed for the above two phases [3,4]. Thermo-physical properties are kept constant in most cases. However more accurate models consider the thermo-physical properties as appropriate functions of hydrogen pressure, concentration, temperature and porosity.

Solution strategies adopted for the modeling of metal hydride reaction beds may be broadly classified into exact and approximate methods. Different numerical schemes adopted for solution include finite difference, finite volume and finite element methods. All these approaches are based on continuum level governing equations. However during the last decade, different microscale and mesoscale methods were used extensively for the better representation of engineering systems. Lattice Boltzmann Method (LBM) is a powerful mesoscale technique for the computational modeling of a wide variety of heat transfer and fluid flow problems in intricate systems. It offers simple, stable and parallelizable algorithm with the capability to handle complicated geometries. However it is not widely reported to simulate the heat and mass transfer in hydride beds.

Askri et al. [5] studied the heat and mass transfer performance of hydrogen storage device with LBM based algorithm. However effect of bed thickness on the sorption performance is not duly addressed. The present paper deals with the study of the hydriding performance of the LaNi₅ based alloy bed with the proposed LBM based algorithm. Effect of different geometric and operating parameters on the sorption performance of the device is studied.

2. THE PHYSICAL MODEL

Figure 1 shows the schematic of the metal hydride storage bed considered in the present study. It is a rectangular alloy bed having four boundary walls. Hydrogen storage material is evenly packed within this storage bed. Hydrogen enters the bed through appropriate filtering and distribution mechanism provided at the top and bottom of the bed. The side walls are duly cooled/ heated with heat exchanger (HX).

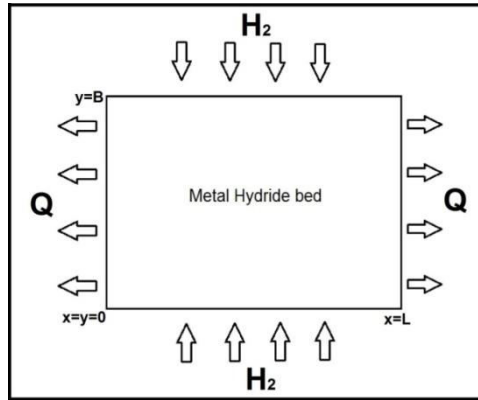


FIGURE 1. SCHEMATIC DIAGRAM OF METAL HYDRIDE BED

Initially, as hydrogen enters the bed, the reaction commences and the temperature of the bed increases due to exothermic heat generation. This heat is transported out of the bed by the heat exchanger and the temperature falls. As the temperature in the vicinity of the heat exchanger is low, the reaction rate will be faster at this location. Therefore, the boundary close to the heat exchanger gets saturated faster. As reaction proceeds, the saturated region progress gradually to the unsaturated region until the bed is fully saturated.

Reiterating the fact that absorption process will be faster in the close vicinity of heat exchanger and it will be saturated earlier than the rest, we can visualize a smooth interface, known as a reaction front which demarcates the fully hydrided portion from the unhydrided/ unsaturated regions. As time proceeds, these reaction fronts move outwards from the periphery of HX to the unsaturated areas of the alloy.

3. PROBLEM FORMULATION

Exact mathematical formulation of heat and mass transfer in metal hydride beds is complicated due to the random nature of bulk material. Hence it is generally assumed that the packed bed is a homogeneous and isotropic porous medium where permeability, effective thermal conductivity and mass diffusivity of the bed are independent of position and direction. The convective heat transfer and inter-particle radiation are negligibly small compared with the conduction heat transfer in the hydride bed. Thermo-physical properties such as density, viscosity, thermal conductivity and specific heat are nearly constant at the pressure, temperature and hydrogen concentration prevailing inside the bed. The equilibrium pressure is determined using van't Hoff's law. Velocity of hydrogen inside the hydride bed is very small as the particle diameter is small compared with the characteristic length.

The governing equations on continuum scale and its equivalent mesoscale formulation using LBM are given in the following sections.

Governing Equations
Mass balance of metal

Conservation of mass for the solid phase of the reactor in the 2D cartesian coordinates is expressed as given below:

$$(1 - \varepsilon) \frac{\partial \rho_s}{\partial t} = \dot{m} + \frac{\partial}{\partial x} \left(D \frac{\partial \rho_s}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial \rho_s}{\partial y} \right) \quad (1)$$

where ρ_s denotes the density of the hydride, D denotes the diffusion coefficient and m represent the rate of hydrogen absorbed within the bed. The second and third terms on the right hand side of the equation represent the diffusive transport due to the concentration gradients existing within the bed.

Reaction kinetics

The amount of hydrogen absorbed is directly related with the reaction rate, and could be given as follows [12]:

$$\dot{m} = -C_a \exp\left(-\frac{E_a}{RT}\right) \ln\left(\frac{P}{P_{eq}}\right) (\rho_{sat} - \rho_s) \quad (2)$$

where C_a is a material dependent constant, E_a is the activation energy of the material, ρ_{sat} is the virtual density of hydride at saturation. The equilibrium pressure is determined by the van't Hoff relationship as given below:

$$\ln P_{eq} = A - \frac{B}{T} \quad (3)$$

where A and B are van't Hoff constants.

Energy balance

Energy conservation equation for the solid phase could be expressed as follows:

$$(1 - \varepsilon)(\rho c)_e \frac{\partial T}{\partial t} = k_e \left\{ \frac{\partial}{\partial x} \left(\frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\frac{\partial T}{\partial y} \right) \right\} + \dot{m} \Delta H^0 \quad (4)$$

The above equation assumes the existence of local thermal equilibrium between the solid and gas within the bed. Hence heat transfer between the two phases is omitted. Radiation heat transfer to the ambient is also neglected. Heat of formation of hydride represents the source term in this equation.

Initial and boundary conditions

Initially the pressure and temperature of hydride bed are assumed uniform and constant. Therefore,

$$\rho = \rho_0 \quad ; \quad p = p_0 \quad ; \quad T = T_0 \quad \text{at} \quad t = 0 \quad (5)$$

The reaction heat is removed from the porous bed using heat transfer media circulated through the heat exchanger. Hydrogen is supplied through porous filter. Convective flux conditions prevail at the filter walls which are assumed to be adiabatic. Based on these, the following boundary conditions are written:

Hydrogen filter wall at $y = 0$ and $y = B$:

$$\frac{\partial T}{\partial y} = 0 \quad \text{at } t > 0 \quad (6)$$

Heat exchanger wall at $x = 0$ and $x = L$:

$$-k \frac{\partial T}{\partial x} = h_f (T_f - T) \quad \text{at } t > 0 \quad (7)$$

Lattice Boltzmann Method

The discrete Boltzmann equations for hydride concentration and temperature with Bhatnagar Gross Krook (BGK) approximation is as given below:

$$f_i(x + e_i \Delta t, t + \Delta t) = f_i(x, t) + \frac{\Delta t}{\tau} \{f_i^{eq}(x, t) - f_i(x, t)\} \quad (8)$$

$$g_i(x + e_i \Delta t, t + \Delta t) = g_i(x, t) + \frac{\Delta t}{\tau} \{g_i^{eq}(x, t) - g_i(x, t)\} \quad (9)$$

These equations can be considered as a combination of collision and streaming steps.

Collision step: During the collision step, the distribution functions are relaxed towards the equilibrium state. The new density distribution function is computed as given below

$$f_i(x, t + \Delta t) = f_i(x, t) + \frac{\Delta t}{\tau} \{f_i^{eq}(x, t) - f_i(x, t)\} + w_i \dot{m} \quad (10)$$

$$g_i(x, t + \Delta t) = g_i(x, t) + \frac{\Delta t}{\tau} \{g_i^{eq}(x, t) - g_i(x, t)\} + \frac{w_i \Delta t S}{(\rho c)_e} \quad (11)$$

where

$$S = \dot{m} \Delta H + k_e \frac{\partial T}{\partial x} \quad (12)$$

where relaxation time

$$\tau = \frac{\Delta t}{\omega} \quad (13)$$

and collision operator

$$\omega = \frac{2(\Delta x)^2}{2\alpha \Delta t + (\Delta x)^2} \quad (14)$$

Streaming step: Particle transfers from one site to another site according to a set of discrete speed in discrete direction are the streaming step.

$$f_i(x + e_i \Delta t, t + \Delta t) = f_i(x, t) \quad (15)$$

$$g_i(x + e_i \Delta t, t + \Delta t) = g_i(x, t) \quad (16)$$

The dependant variables (ρ and T) can be calculated from the respective distribution functions as given below.

$$\rho(x,t) = \sum_{i=1}^n f_i \quad (17)$$

$$T(x,t) = \sum_{i=1}^n g_i \quad (18)$$

The equilibrium distribution function can be written as

$$f_i^{eq}(x,t) = w_i \rho(x,t) \quad (19)$$

$$g_i^{eq}(x,t) = w_i T(x,t) \quad (20)$$

Mirror reflection scheme is used for the representation of boundary conditions.

4. SOLUTION METHODOLOGY

The LBM algorithm is implemented in MATLAB commercial code. The important steps are given below.

1. The computational domain is divided into finite number of lattices as shown in Fig. 2. As grid size affect simulation results, the domain is divided into an economic grid size of 150x150, after conducting grid independence test.
2. Set initial values of hydrogen concentration and temperature.
3. Evaluate the equilibrium distribution functions based on initial values of density and temperature.
4. Evaluate the new equilibrium distribution function after H₂ sorption at the respective lattice sites (collision step).
5. Heat/mass diffusion across lattice sites (streaming)
6. Compute new hydrogen concentration and temperature.
7. Evaluate new equilibrium distribution functions and proceed as given above
8. Repeat the process till steady state.

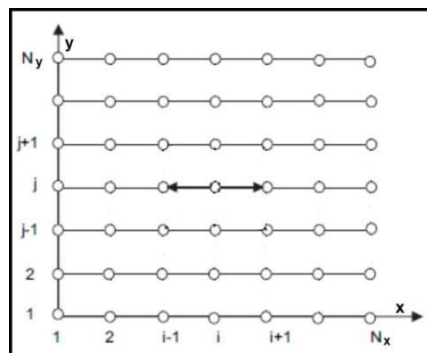


FIGURE 2. DISCRETIZATION OF THE COMPUTATIONAL DOMAIN

5. COMPARISON OF RESULTS

Prior to the discussion of salient results, the results of LBM algorithm is compared with the corresponding results of FEM based Comsol MultiphysicsTM. Figure 3 shows reasonable agreement between the two methods and the later numerical model is already validated with the results from experiments [6].

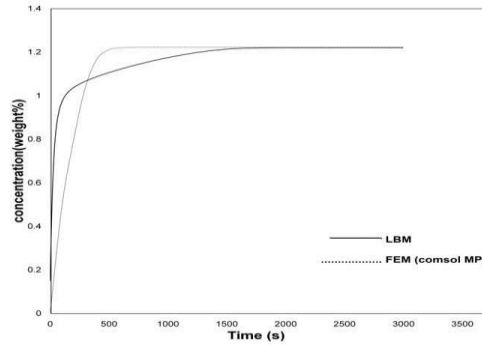


FIGURE 3. HYDRIDING OF THE ALLOY BED-COMPARISON OF LBM WITH FEM BASED COMSOL MULTIPHYSICS™

6. RESULTS

LaNi₅ is selected as the hydriding material for the present simulation. The reaction rate of LaNi₅ is extremely fast and the alloy performance is limited by heat transfer in most applications. Role of intrinsic chemical kinetics is limited. So the selection of LaNi₅ as the hydriding alloy in the present case is prudent in comparison with many other alloys. Reaction kinetics and thermo-physical property data of LaNi₅ and hydrogen are readily available in literature and are summarized in Table 1. Parameter ranges used in simulation are given in Table 2.

TABLE 1. THERMO-PHYSICAL PROPERTIES OF LaNi₅ and H₂ [3,4]

| Parameter | LaNi ₅ | Hydrogen |
|--|-------------------|---------------|
| Density, kg m ⁻³ | 8200 | 0.0838 at NTP |
| Specific heat, Jkg ⁻¹ K ⁻¹ | 419 | 14,890 |
| Eff. thermal conductivity, Wm ⁻¹ K ⁻¹ | 1.2 | 0.12 |
| Activation energy (Abs.), E _a J mol ⁻¹ | 21170 | - |
| Activation energy (Des.), E _d J mol ⁻¹ | 16420 | - |
| Constants Eq. (3.9-3.11): C _a , s ⁻¹ | 59.187 | - |
| A | 12.99 | - |
| B | 3704.59 | - |

TABLE 2. PARAMETER VALUES USED IN SIMULATION

| Parameter | Range of values |
|--|-----------------|
| Initial temperature of hydride bed, K | 293 (Constant) |
| Supply pressure of hydrogen, bar | 7-15 |
| Coolant temperature, K | 290-320 |
| Ov. heat transfer coefficient, W m ⁻² K ⁻¹ | 500 (constant) |
| Porosity | 0.5 (Constant) |
| Bed thickness, mm | 10 – 20 |

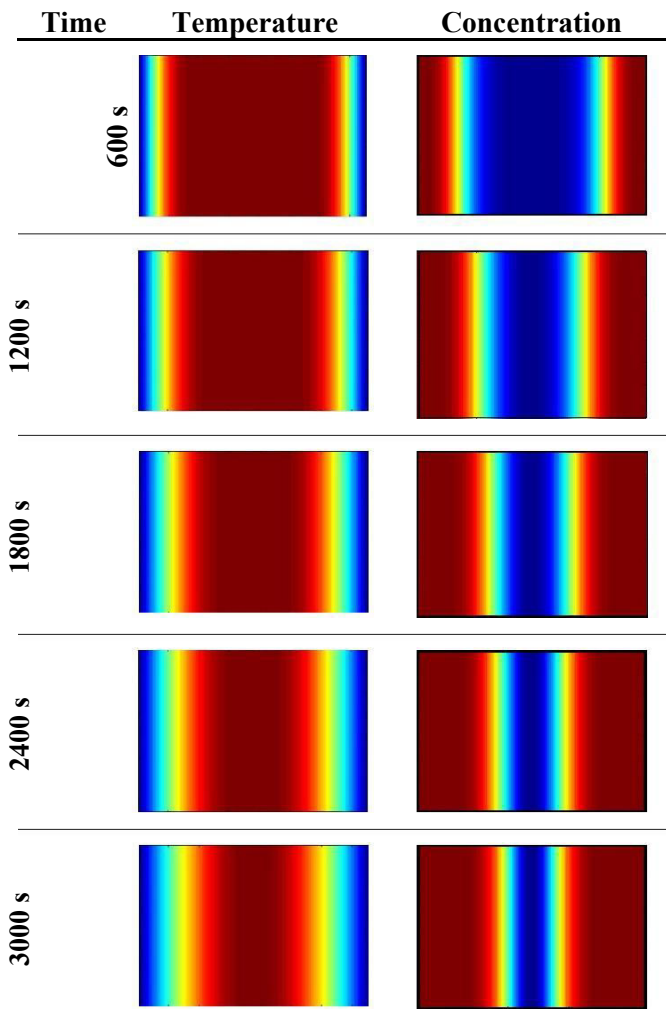


FIGURE 4. EVOLUTION OF TEMP. AND CONC. IN HYDRIDE BED AT DIFF. TIME INTERVALS ($T_f = 300$ K, $P = 15$ bar, $h = 500$ W/m²-K)

The main parameters which influence the mass transfer process in the hydride bed include the hydrogen gas pressure, hydrogen equilibrium pressure, hydride bed temperature and the hydrogen concentration in the hydride. A large amount of heat is generated due to the exothermic reaction, forming hydride. The reaction within the bed is proportional to the pressure gradient between the gas supply pressure and equilibrium pressure corresponding to the bed temperature. While the supply pressure remains constant, the reaction is vigorous when the bed temperature and the corresponding equilibrium pressure are lower. The bed temperature increases rapidly during the initial phase of the reaction. Heat transfer from the bed to the cooling media dissipates the heat generated from the process. As thermal resistance increases with time, hydriding rate decreases.

Figure 4 shows the variation of temperature and concentration with time for a typical case. Reaction rate is faster in the vicinity of the heat exchanger. Away from the HX wall, the bed temperature rises rapidly to a peak value and decreases slowly. Hydriding alloy requires large temperature gradients to conduct the heat of reaction to the heat exchange media due to its low thermal conductivity. The high temperatures

prevailing farther from the heat exchanger surfaces increase the corresponding equilibrium pressure, thereby reducing the reaction rate. Hence, faster reaction rates are observed in the vicinity of the heat exchanger wall leading to higher saturation levels. As reaction proceeds, the reaction front progresses from the heat exchanger walls to the unsaturated areas within the bed.

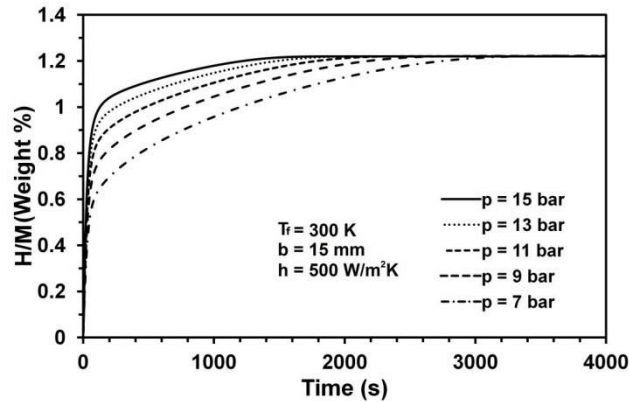


FIGURE 5. EFFECT OF HYDROGEN SUPPLY PRESSURE ON HYDROGEN ABSORPTION

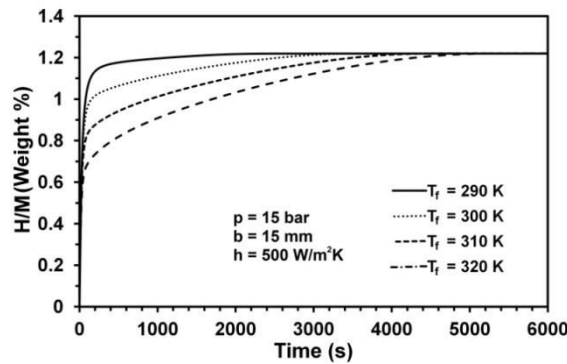


FIGURE 6. EFFECT OF COOLANT TEMPERATURE ON HYDROGEN ABSORPTION

Hydrogen supply pressure, coolant temperature and coolant side heat transfer coefficient are independent operational parameters which influence the performance of the hydride bed. Supply pressure is an important operating parameter controlling the hydriding rates

because the differential between equilibrium pressure and imposed pressure within the reactor controls the absorption process. A higher pressure differential reduces the elapsed time for hydriding as shown in Fig. 5. Two other parameters namely, coolant temperature and coolant side heat transfer coefficient control the transport of exothermic heat generated within the bed. Effect of coolant temperature on hydriding is shown in Fig. 6. At any given supply pressure, lower coolant temperature causes a lower bed temperature and thereby lower equilibrium pressure. It consequently increases the driving potential for mass transfer, resulting in a higher rate of reaction.

Figure 7 shows the influence of bed thickness on absorption of hydrogen. In all cases, the same saturated state of about 1.2 weight % H_2 is achieved after different time intervals. It is obvious that, at lower bed thicknesses the hydride bed reaches saturation earlier. Higher bed thicknesses follow a flatter profile and reach the saturation state much later. Higher bed temperature, lower reaction rate, larger conduction path length and low thermal conductivity of the material collectively contribute to this behaviour. For a given

bed thickness, heat transfer as well as reaction kinetics are jointly important in determining the absorption time. As reaction kinetics is more material dependent, for a specified effective thermal conductivity value, there exists an optimum bed thickness satisfying the performance and system weight.

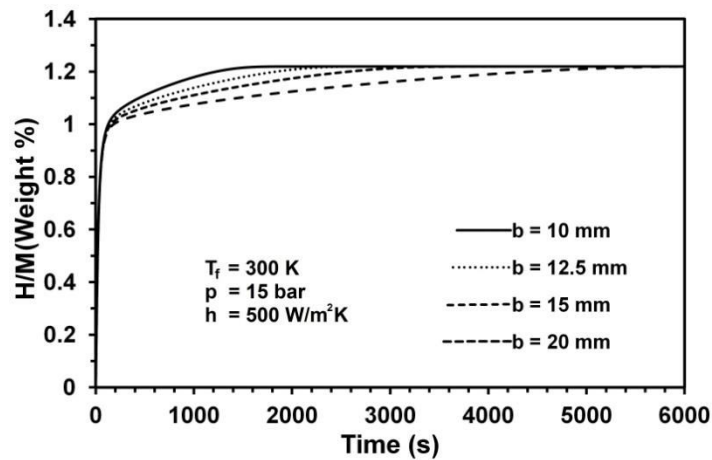


FIGURE 7. EFFECT OF BED THICKNESS ON HYDROGEN ABSORPTION

7. CONCLUSIONS

Sorption performance of LaNi₅ based hydrogen storage bed is simulated using Lattice Boltzmann Method. The simulations were carried out for suitable ranges of geometric and operating parameters. Results of the simulation reiterate the importance of bed thickness as the important geometric parameter which controls the hydriding rate in the metal hydride bed. The hydrogen supply pressure and coolant temperature are the important operating parameters influencing the charging rate.

The LBM code is simple and computationally efficient. The results are in good agreement with the corresponding results of FEM based COMSOL MultiphysicsTM.

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