



NUMERICAL ANALYSIS OF HYDROGEN ABSORPTION IN A POROUS METAL BED

Muhittin BİLGİLİ, Mahmut D. MAT* and Ö. Ercan ATAER¹

Gazi University, Mechanical Engineering Department, Maltepe, 06570 Ankara, Turkey

Niğde University, Mechanical Engineering Department, 51100 Niğde, Turkey

E-Mail : bilgili@gazi.edu.tr; mdmat@nigde.edu.tr; oataer@gazi.edu.tr

(Geliş Tarihi : 03.04.2003)

Abstract: Two dimensional heat and mass transfer are analyzed for hydrogen absorption in a porous metal bed using cylindrical coordinates. For high cooling rates an annular geometry is selected for the porous metal bed, and the bed is cooled by fluid on both internal and external surfaces. Absorption process is analyzed numerically for the porous LaNi₅ metal bed. The variations of the metal hydride temperature and hydrogen/metal atomic ratio are calculated in the radial and axial directions by using a Computational Fluid Dynamics (CFD) program. It has been found that hydride formation takes places near the cold boundaries. The results were also compared with the numerical outcomes given in the literature for different geometries.

Key words: Hydrogen Absorption, Hydrogen Energy, Numerical Analysis, Hydride Beds and Mathematical Model.

GÖZENEKLİ METAL YATAKLARDA HİDROJEN SOĞURULMASININ SAYISAL MODELLENMESİ

Özet: Gözenekli metal yataklarda hidrojen gazının soğurulması, iki boyutlu olarak ısı ve kütle transferi yönünden silindirik koordinatlarda analiz edilmiştir. Yüksek soğutma oranı için eş merkezli iki silindir arasındaki gözenekli metal ortam seçilmiştir ve metal yatak, iç ve dış yüzeylerden akışkan ile soğutulmuştur. Gözenekli metal ortam olarak, LaNi₅ metal yatak seçildi ve hidrojen soğurulması sayısal olarak analiz edilmiştir. Radyal ve eksenel yönlerde metal hidrid sıcaklık değişimleri ve hidrojen/metal oranları bir Sayısal Akışkanlar Mekaniği (SAD) programı kullanılarak hesaplanmıştır. Hidrid oluşumu soğuk yüzeyler üzerinde daha hızlı şekilde meydana geldiği görülmüştür. Sonuçlar literatürde verilen farklı geometrilerdeki sonuçlar ile karşılaştırılmıştır.

Anahtar kelimeler: Hidrojen Absorpsiyonu, Hidrojen Enerjisi, Sayısal Analiz, Hidrid Yatak, Matematik Model.

¹ Author to whom correspondence should be addressed.

NOMENCLATURE

a_k	the combined advection and diffusion coefficients
a_o	coefficient due to transient advection
C_p	specific heat (J/kg.K)
E_a	activation energy (J/mol)
h	heat transfer coefficient (W/m ² K)
H/M	hydrogen and metal atomic ratio
ΔH	heat of reaction (J/mol)
K	thermal conductivity (W/m.K)
m	mass of hydrogen absorption rate (kg/m ³ .s)
M	molecular weight (kg/mol)
P	pressure (Pa)
r	radial direction (m)
r_i	inner diameter (m)
r_o	outer diameter (m)
R	gas constant (J/kg.K)
L	length of the metal bed (m)
r	radial direction (m)
t	time (s)
T	temperature (K)
V	gas velocity (m/s)
u_r	radial component of the gas velocity (m/s)
u_z	axial component of the gas velocity (m/s)
ρ	density (kg/m ³)
ϕ	generic variable
ϕ_p	unknown nodal value

Subscripts

e	effective
eq	equilibrium
f	cooling fluid
g	gas
o	initial
s	solid
sat	saturated

INTRODUCTION

Hydrogen energy appears to be the best alternative for the future to replace the fossil fuels, and it has a wide field of industrial applications. There are theoretical and experimental investigations in literature on several aspects of hydride storage methods. It is well known that the hydride formation takes place faster on the cold boundaries, and therefore the reactor bed should have wide heat transfer area.

Gopal and Murthy (1992) developed a one-dimensional mathematical model for heat and mass transfer in metal hydride bed of annular cylindrical configuration. While the hydrogen is charged on the inner surface of the duct axially, the bed is cooled

on the outer surface of the duct by a fluid. Their results cover a wide range of alloys and operating conditions. They used the results to obtain the correlations for space-average temperature and concentration in terms of bed properties and operating parameters. They demonstrated the use of these correlations using a $\text{LaNi}_{4.7}\text{Al}_{0.3}$ bed.

Gopal and Murthy (1995) also carried out experiments on a cylindrical metal hydride reactor filled with $\text{MmNi}_{4.5}\text{Al}_{0.5}$ powder. The performance of the reactor during absorption and desorption is tested at different coolant temperatures. Good agreement is obtained between the experimental and predicted heat and mass transfer rates despite some discrepancies in the bed temperatures.

Mat and Kaplan (2001) studied the metal hydride formation in a $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ porous metal bed storage tank numerically. Their cylindrical model with a finite length, considers heat, mass transfer and chemical reaction in the bed. They have shown that the absorbed hydrogen mass increases fast at the initial times of the hydriding process and slows down after the temperature of reaction bed increases due to heat of reaction. Their numerical results agree satisfactorily with the experimental data given by Mayer *et al* (1987).

Aldaş, *et al* (2002) investigated the heat and mass transfer, the fluid flow and chemical reactions in a hydride bed numerically with a general purpose PHOENICS code. They observed that the hydride formation takes place faster near the cooled boundary walls and slower around the core region of the bed. It is found that fluid flow affects the temperature distribution in the system. However, it does not significantly improve the amount of hydrogen absorbed.

Mat and Kaplan (2001), and Aldaş and Mat (2002) analyzed the hydrogen charge in the metal bed and subsequent hydriding processes in a cylindrical porous metal bed. The tank is of 25 mm radius and 60 mm height and filled with porous LaNi_5 alloy. Numerical results show that hydrogen absorption is completed faster near the cooled wall, while it takes longer at the center.

In this study an annular porous-metal bed is selected as shown in Figure 1. Considering the importance of the cooling rate, the metal bed is cooled on the internal and external surfaces of the annular duct. Hydrogen is charged in axial direction. Various materials like B, Mg and LaNi_5 can be used for the metal beds. In this study, however, only the absorption by the LaNi_5 was considered.

BASIC EQUATIONS

The heat and mass transfer and chemical reaction equations within the hydrogen storage bed and on the surfaces of the bed are the basic equations. For hydrogen, the two dimensional conservation of mass in cylindrical coordinates is written as

$$\varepsilon \frac{\partial \rho_g}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r \rho_g u_r) + \frac{\partial}{\partial z} (\rho_g u_z) = -\dot{m} \quad (1)$$

where ε is the porosity. Conservation of mass of porous storage bed is written as

$$(1 - \varepsilon) \frac{\partial \rho_s}{\partial t} = \dot{m} \quad (2)$$

Darcy's law is used in the analysis to calculate the gas velocities

$$u = -\frac{K}{\mu_g} \nabla P_g \quad (3)$$

where K is the permeability of the porous medium and μ_g is the molecular viscosity of hydrogen.

The energy balance equation is written as

$$\begin{aligned} (\rho C_p)_e \frac{\partial T}{\partial t} = & \frac{1}{r} \frac{\partial}{\partial r} \left(r k_e \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(k_e \frac{\partial T}{\partial z} \right) \\ & - (\rho_g C_{pg} u_r) \frac{\partial T}{\partial r} - (\rho_g C_{pg} u_z) \frac{\partial T}{\partial z} \\ & - m(\Delta H - T(C_{pg} - C_{ps})) \end{aligned} \quad (4)$$

where u_r and u_z are the velocity components in r and z directions respectively. ρ_e , C_{pe} , k_e , $\dot{m}$ and ΔH are effective density, specific heat, thermal conductivity, mass rate of hydrogen absorption and heat of reaction respectively. $(\rho C_p)_e$ is written as

$$(\rho C_p)_e = (\varepsilon \rho_g C_{pg} + (1 - \varepsilon) \rho_s C_{ps}) \quad (5)$$

Effective thermal conductivity of the porous storage bed is calculated using (Jemni *et al*, 1999);

$$k_e = \varepsilon k_g + (1 - \varepsilon) k_s \quad (6)$$

where k_g and k_s are the thermal conductivity of the gas and solid phases respectively. Jemni and Nasrallah (1995) has shown that the mass of

hydrogen absorption is related to the reaction rate and defined it by the expression written as

$$\dot{m} = -C_a \exp \left(-\frac{E_a}{RT_s} \right) \ln \left(\frac{P_g}{P_{eq}} \right) (\rho_{ss} - \rho_s) \quad (7)$$

where C_a is the material constant, ρ_{ss} is the density of hydrogen saturated solid and ρ_s is the density of the solid phase, and P_{eq} is the equilibrium pressure and calculated using Van't Hoff equation that is

$$\ln P_{eq} = A - \frac{B}{T} \quad (8)$$

where A and B are dimensionless and dimensional material constants. Jemni *et al* (1999) proposed the values of A and B as 100.75 and 31896.25 K for LaNi₅, respectively.

Initial and Boundary Conditions

It is assumed that initially the porous metal bed and gas have constant temperature and pressure;

$$\rho_g = \rho_{g0}, \rho_s = \rho_{s0}, P = P_0, T = T_0, u_z = 0 \text{ at } t = 0 \quad (9)$$

Annular storage bed is cooled by liquid coolant at the temperature of T_f and it is charged within the interval of $r_o > r > r_i$ at constant pressure. Then the boundary conditions can be written as:

$$P = P(z, t) \text{ and } T = T(r, z, t)$$

$$\frac{\partial P}{\partial z}(L, t) = 0 \text{ and } \frac{\partial T}{\partial z}(r, L, t) = 0 \quad (10)$$

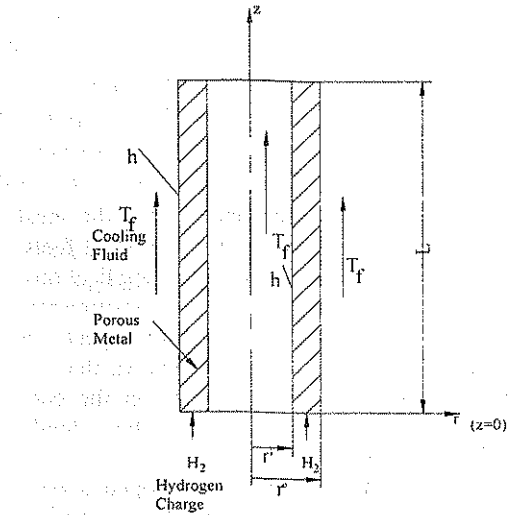


Figure 1. The porous metal bed.

There are convective boundary conditions on the internal and external surfaces of the annular porous hydride bed. The convective boundary conditions can be written as

$$-k \frac{\partial T}{\partial r}(r_i, z, t) + hT(r_i, z, t) = hT_f \quad (11)$$

$$-k \frac{\partial T}{\partial r}(r_o, z, t) + hT(r_o, z, t) = hT_f \quad (12)$$

$$-k \frac{\partial T}{\partial z}(r, 0, t) + h_{z=0}T(r, 0, t) = h_{z=0}T_{H_2} \quad (13)$$

where h is the heat transfer coefficient on the inner and outer surfaces of the hydride bed and taken as equal to each other.

At the entrance of hydrogen to the metal bed the other convective boundary condition exists. This boundary condition is seen in equation (13).

Mathematical Model

Schematic representation of the porous metal bed is given in Figure 1. Porous metal bed inner radius and outer radius were selected as 10 mm and 20 mm, respectively. In addition, length of the porous metal bed was 30 mm. The mesh point distribution of the porous metal bed is shown in Figure 2. Hydrogen is charged to the porous metal bed from the bottom surface. Considered system is axially symmetric and during the solution, first of all cell size independence test was applied to the system. Different cell distributions have been tried, and r direction was divided into 20 cells and z direction was divided into 60 cells. In the solution of the problem, number of the mesh points near the boundaries was much more than the cells at the middle of the cylinder. Because of this inequality in cell distribution, cell centers were in different positions and therefore geometric ratios were in different proportions.

NUMERICAL METHOD

The method of solution involves the integration of the governing differential equations over finite control volume and transforming them into a general algebraic form, defined as:

$$a_p \phi_p = \sum a_k \phi_k + a_o \phi_p^o + b \quad (13)$$

where ϕ represents a generic variable (T, u_r, u_z), ϕ_p is the unknown nodal value, ϕ_p^o is ϕ_p at an earlier time, a_o is a coefficient due to transient advection, a_k represents the advection coefficients and b is a component of the linearized source term.

This system of linearized equations is solved by a guess and correct (SIMPLE) algorithm. PHOENICS is used for the solution and it allows the user to add the source terms that do not exist in the program with a code suitable to the logic of the main program (Versteeg and Malalasekera, 1996).

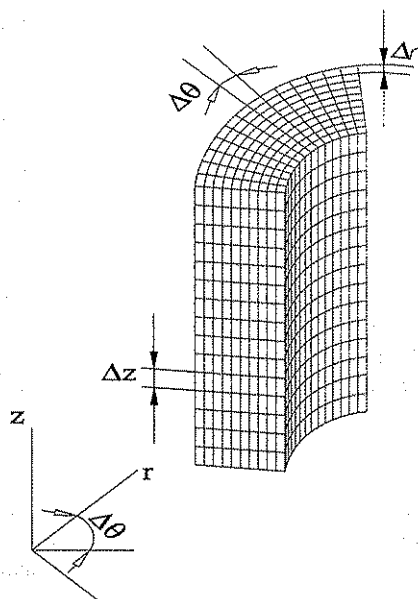


Figure 2. The cell distribution of porous metal bed.

Table 1. The properties of LaNi_5 and Hydrogen used in the analysis

LaNi_5	
Density, ρ (kg/m^3)	4200
Specific heat, C_p (J/kg.K)	419
Thermal conductivity, k (W/m.K)	1.087
Heat of reaction, ΔH (J/mol H_2)	-10
Hydrogen	
Density, ρ (kg/m^3)	0.0838
Specific heat, C_p (J/kg.K)	14.89
Thermal conductivity, k (W/m.K)	0.761147×10^{-4}

The heat transfer coefficients were assumed constant. While the heat transfer coefficient on the entrance of hydrogen to the metal bed was taken as $50 \text{ W/m}^2\text{K}$, the heat transfer coefficient on the

inner and outer surfaces of the duct were taken as $500 \text{ W/m}^2 \cdot \text{K}$.

RESULTS

The properties of LaNi_5 and Hydrogen used in the analysis were assumed to be constant during the numerical analysis and are given in Table 1. In the analysis, the inlet temperature of the hydrogen and the initial temperature of the metal hydride bed were assumed as 20°C . The transient behavior of the metal hydride bed is obtained and given in the figures below.

Variation of temperature of the metal hydride bed with time at the radial locations of 0.01073, 0.01466, 0.01884 m are given for the z/L ratios of 0.1807, 0.602 and 0.950 in Figures 3, 4 and 5 respectively.

Figure 3 is for the z/L ratio of 0.1807, and since the metal hydride bed is cooled on both internal and external surfaces, the temperatures corresponding to $r=0.01073 \text{ m}$ and $r=0.01884 \text{ m}$ are lower than the middle radial location of $r=0.01466 \text{ m}$. The small temperature difference between $r=0.01073 \text{ m}$ and $r=0.01884 \text{ m}$ radial locations is mainly due to difference between the heat transfer areas of the inner and outer surfaces of the duct.

As seen on the figures the variations of temperature with time at different radial locations show similar behavior. At $r=0.01466 \text{ m}$ the temperature of the metal hydride bed reaches a maximum temperature of 329.5 K at the charging time of 110 s . The temperature difference between the inner ($r=0.01466 \text{ m}$) and outer ($r=0.01884 \text{ m}$) radial positions of metal hydride bed is about 3 K as shown in Figure 3. The temperature difference between the radial locations decreases with time and approaches to zero at about 1500 s .

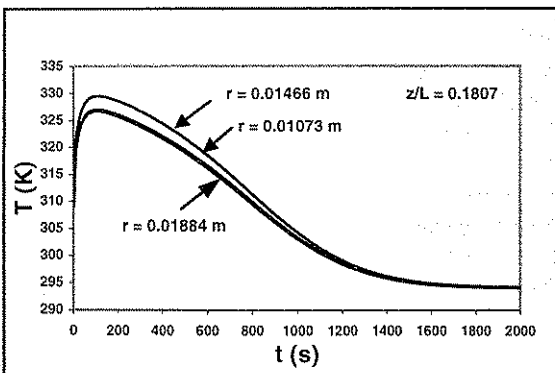


Figure 3. Variation of the metal-bed temperature with time at $z/L = 0.1807$ and different radial location

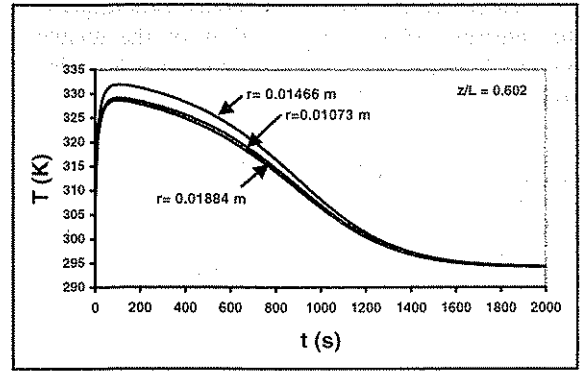


Figure 4. Variation of the metal-bed temperature with time at $z/L = 0.602$ and different radial locations.

When the hydrogen charge starts, the heat is generated due to absorption in the metal bed, and the temperature of the metal bed increases. The heat is transferred by conduction to the inner and outer surfaces of the duct in radial direction and also in the axial direction. The temperature starts to drop when the absorption is completed.

Variation of metal-bed temperature with time at the axial positions of $z/L = 0.18, 0.60$ and 0.95 are calculated for the radial positions of $r = 0.01073, 0.01466$ and 0.01884 m and given in Figures 6, 7 and 8, respectively.

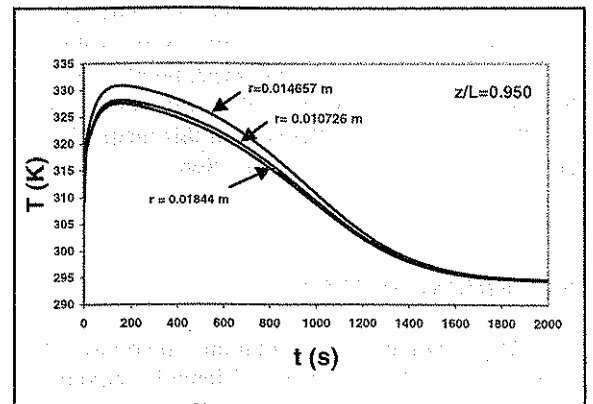


Figure 5. Variation of the metal-bed temperature with time at different radial locations and at $z/L = 0.95$.

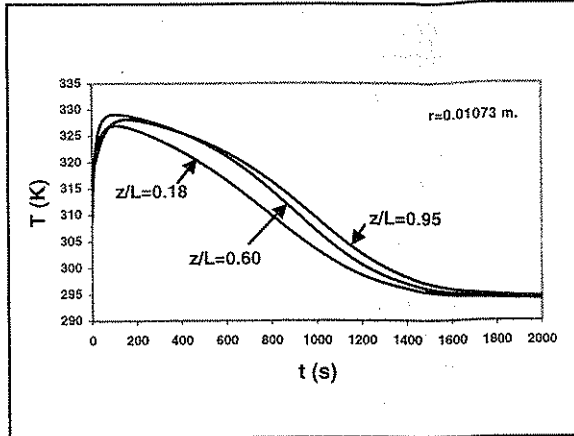


Figure 6. Variation of the metal-bed temperature with time at different axial locations and at $r = 0.01073$ m.

At the radial position of $r=0.01073$ m, the variation of the temperature with time is low at low z/L ratios. Similar temperature time curves are obtained at the radial locations of 0.01466 and 0.01884 m.

The maximum temperatures and the corresponding times are given in Table 2 at different z/L ratios and r -values. As indicated above, the maximum temperatures are obtained

Table 2. The maximum temperatures and corresponding times.

Z/L	0.18		0.60		0.95	
	$T_{\max}$ (K)	t (s)	$T_{\max}$ (K)	t (s)	$T_{\max}$ (K)	t (s)
$r = 0.01073$ m	326.9	108	329.1	104	328.1	156
$r = 0.01466$ m	329.5	110	331.9	106	330.8	160
$r = 0.01884$ m	326.7	104	328.6	102	327.5	154

at locations far from the cooled surfaces in radial direction and at initial time values of the process. The maximum temperature of 331.9 K is obtained at $r=0.01466$ m and at the z/L ratio of 0.60. It is interesting that the maximum temperature is obtained at the z/L ratio of 0.6 among three selected values, and this may be due to the axial conduction.

Figure 10 shows that the H/M ratio decreases gradually in axial direction at an earlier time (500s) and reaches a constant value when the hydrogen formation is completed eventually.

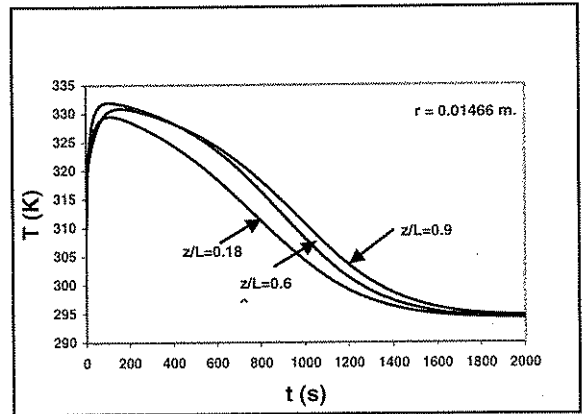


Figure 7. Variation of the metal-bed temperature with time at different axial locations and at $r = 0.01466$ m.

For different axial z/L values variation of the hydrogen and metal atomic ratio (H/M) at the radial location of $r=0.01466$, is shown in Figure 9.

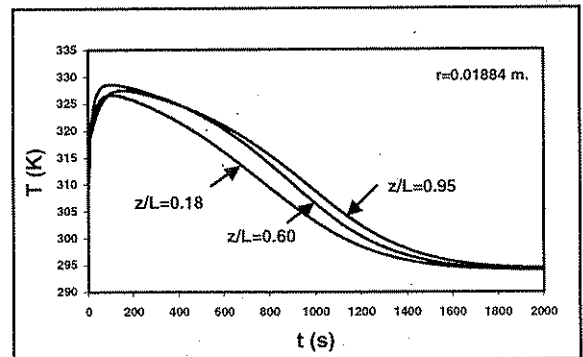


Figure 8. Variation of the metal-bed temperature with time at different axial locations and at $r = 0.01884$ m.

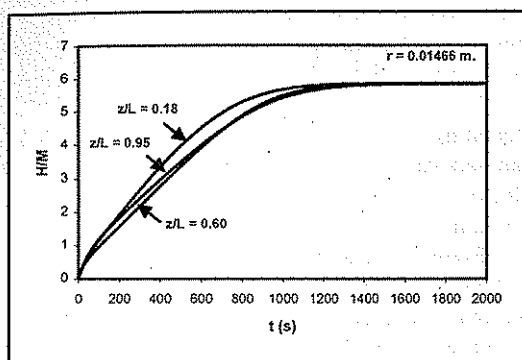


Figure 9. Variation of H/M with time at different z/L values and at $r=0.01466$ m.

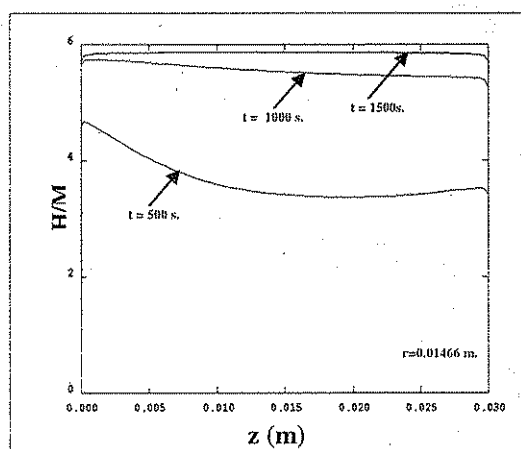


Figure 10. Variation of H/M with axial direction at different time values.

In Figure 11, the H/M ratio is high near the boundaries of metal bed. It shows that high cooling rates of the metal bed increases the absorption rate. The hydride formation is minimum near to $r=0.0145$ m at $t=500$ seconds in Figure 11, because of the low cooling effect.

CONCLUSIONS

The hydrogen absorption in an annular LaNi_5 metal-hydride bed is investigated numerically, and PHOENICS is used for the numerical solution.

The numerical results show that the high cooling rates of porous LaNi_5 metal bed can be obtained using the proposed geometry in this study. The high cooling rates increases the hydrogen-absorption rate up to about $H/M=6$. Further increase is, however, limited due to the low thermal conductivity of the porous LaNi_5 , i.e. 1.087 W/m.K.

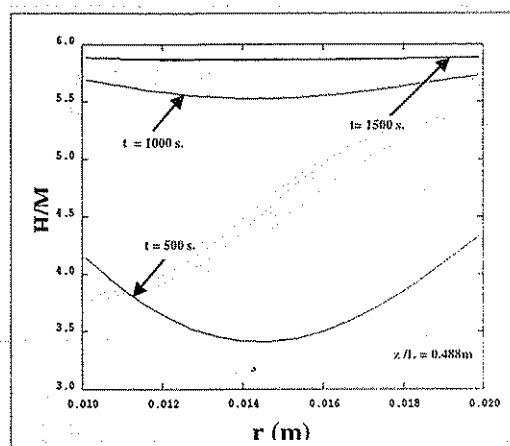


Figure 11. Variation of H/M with radial direction at different time values.

The proposed geometry in this study has higher hydrogen absorption rate in comparison to the solid-cylinder configuration cooled from the outer surface only as reported by Mat and Kaplan (2001), and Aldaş, *et al* (2002) and to annular cylindrical configuration proposed by Gopal and Murthy (1992), in which the hydrogen was charged on the inner surface of the duct axially, and the bed was cooled through the outer surface of the duct by a fluid.

Consequently, it can be stated that the high hydrogen-absorption rate can be obtained by the porous metal bed that has high thermal conductivity and specific heat, and by the geometry with high cooling rate as proposed in this work.

REFERENCES

- Aldaş, K., Mat, M., Kaplan, Y., "A three-dimensional mathematical model for absorption in a metal hydride bed", *Int. J. Hydrogen Energy*, 27(10), 1049-1056, 2002.
- Aldaş, K., Mat, M., "Numerical analysis of hydrogen storage in metal-hydride beds", *Turkish J. of Engineering and Environmental Science*, 26, 201-207, 2002.
- Gopal, M.R., Murty, S.S., "Prediction of heat and mass transfer in annular cylindrical metal hydride beds", *Int. J. Hydrogen Energy*, 17(10), 795-805, 1992.
- Gopal, M.R., Murty, S.S., "Studies on Heat and mass transfer in metal hydride beds", *Int. J. Hydrogen Energy*, 20(11), 911-917, 1995.

Jemni, A., Ben Nasrallah, S., "Study of two-dimensional heat and mass transfer during absorption in a metal-hydrogen reactor", *Int. J. Hydrogen Energy*, 20(1), 43-52, 1995.

Jemni, A., Ben Nasrallah, S., Jilani L. "Experimental and theoretical study of a metal-hydrogen reactor", *Int. J. Hydrogen Energy*, 24(7), 631-644, 1999.

Mat, M., Kaplan, Y., "Numerical Study of hydrogen absorption in an LaNi_5 hydride reactor", *Int. J. Hydrogen Energy*, 26(9), 957-963, 2001.

Mayer, U., Groll M., and Supper, W., "Heat and mass transfer in metal hydride reaction beds: Experimental and Theoretical Results", *J of Less-Common Metals*, 131, 235-44, 1987

Versteg, H. K. and Malalasekera, W., *An Introduction to Computational Fluid Dynamics, "The Finite Volume Method"*, 1996.