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Numerical simulation and performance test of metal hydride hydrogen storage system

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Abstract
Metal hydride reactors are widely used in many industrial applications, such as hydrogen storage, thermal compression, heat pump, etc. According to the research requirement of metal hydride hydrogen storage, the thermal analyses have been implemented in the paper. The metal hydride reaction beds are considered as coupled cylindrical tube modules which combine the chemical absorption and desorption in metal hydride. The model is then used metal hydride $LaNi_5$ as an example to predict the performance of metal hydride hydrogen storage devices, such as the position of hydration front and the thermal flux. Under the different boundary condition the characteristics of heat transfer and mass transfer in metal hydride have influence on the hydrogen absorption and desorption. The researches revealed that the scroll design can improve the temperature distribution in the reactor and the porous tube for directing hydrogen can increase the penetration depth of hydride reaction to decrease the hydrogen absorption time.

Keywords: Metal hydride reactor, Hydrogen storage system.

1. Introduction

The energy supply to the humankind in the last two centuries was solely based on fossil fuels such as coal in the 19th century and crude oil and natural gas in the 20th century. Unfortunately, this fossil fuel-based economy has led us to face the situation such as global warning, climate changing and exhausted resources. The hydrogen economy offers a potential solution to satisfy the global energy requirements while reducing greenhouse emissions and improving energy security. Hydrogen storage is definitely one of the key challenges in developing hydrogen economy.

Metal hydrides are applied for reversible solid-state hydrogen storage at low pressures and with high volumetric capacity. One possible application for metal hydrides is as storage medium in hydrogen stand-alone power systems. The heat energy exchange required during the absorption and desorption is quite large. For example, per mole of hydrogen gas for $LaNi_5$ [1] is about -30.8 kJ and for MgH_2 [2] is about -75.0 kJ. The metal hydrides AB_5 group has low thermal conductivity and is about 0.1 W m^{-1} K^{-1} [3]. Therefore, the temperature affects the reaction rate greatly through both driving force and chemical activation [4].

Yang et al. [5] recommended that as the reaction proceeds, the heat must be managed properly and the heat transfer and heat loss issues are recognized as important in the design of metal hydride reactors. The

performance of the reactor deserves careful study and is greatly influenced by its design. The reaction beds with different heat conduction matrices to enhance the thermal conductance of the reaction bed have been investigated by Groll et al. [6, 7]. The employed heat conduction matrices include porous aluminum foam with porosity 90%, corrugated copper band, corrugated perforated aluminum band and copper cassette. Dhaou et al. [8] used the finned heat exchange system inside the reactor and revealed that the absorption/desorption times were considerable reduced.

A great amount of simulation studies have been reported on the heat and mass transfer process in a metal hydride bed. From Jemni and Ben Nasrallah [9, 10] studies, two dimensional heat and mass transfer within a metal hydride reactor for both absorption and desorption processes were investigated. Mat et al. [11] and Aldas et al. [12] studied numerically three-dimensional heat and mass transfer in a metal hydride bed during absorption.

Thus, the objectives of the paper are to compare the temperature distribution inside reactor between the scroll design reactor and original reactor. The temperature distribution has influence on hydrogen absorption obviously. The effect of porous tube for directing hydrogen into reactor also is discussed from the simulation results.

2. Numerical model and analysis

The hydride reaction beds are considered as coupled cylindrical tube modules in the simulation and is shown in Figure 1. Hydrogen flows directly from the center of a circle of hydrogen storage canister and then distributes inside the metal hydride powder along the axial direction. When the hydrogen is initially introduced in the inner layer ($r=r_{inner}$) of metal hydride reactor, a solid solution (α-phase) region is observed as the hydrogen absorption process. After certain amount of the hydrogen is introduced, the lattice is saturated with hydrogen atoms and second phase (β-phase) begins to appear. The middle layer ($r=r_{front}$) of metal hydride reactor is the position of the hydration front. The outer layer ($r=r_{outer}$) of metal hydride reactor is responsible for supporting the metal hydride powder and thermal management.

The heat and mass transfer model through metal hydride beds is a complicated phenomenon and heat transfer models including conduction, convection and radiation. The study tried to understand the heat transfer coefficient effect on the absorption/desorption ability through the simulation predictions. The tradition gas transport equation in porous media is to describe the mass transfer in the metal hydride bed. By solving the Darcy equation can obtain the diffusion behavior of hydrogen in metal hydride bed. The detail thermal modeling and analysis of a metal hydride is as the following [13].

Livenstov [14] proposed the quasi-stationary method to obtain the simplified model of a metal hydride module. The stationary filtration equation in cylindrical coordinates is

$$\frac{\partial}{\partial r}\left[P\frac{\partial P}{\partial r}\right]+\frac{1}{r}P\frac{\partial P}{\partial r}=0 \tag{1}$$

The solution is solved as

$$P=A_1\ln r+A_2 \tag{2}$$

The hydrogen flux to the hydration front according to the Darcy law is given by

$$J_f=-\sigma\left(\frac{P}{T}\frac{\partial P}{\partial T}\right) \tag{3}$$

According to the Artemenko et al [15], σ in the Eq. (3) is

$$\sigma=\frac{1}{2}D\frac{\varepsilon^3}{\mu}\left(\frac{d}{1-\varepsilon}\right)^2 M_{H_2}\frac{1}{\widetilde{R}} \tag{4}$$

where R is gas constant, D is empirical coefficient for filtration and D=0.00237 is for $LaNi_5$. The term ε and d are the porosity of metal hydride and average diameter of metal hydride particle, respectively. In the meanwhile, J_f is hydrogen flux and determined by the hydration front velocity $\dot{r}_f$ and can be written as

$$J_f=-\delta\ddot{r}_f \tag{5}$$

$$\delta=\frac{c_{\max}-c_0}{2M_m}\rho_m M_{H2} \tag{6}$$

Equalizing Egs. (3) and (5) gives

$$\frac{\sigma}{T_f}\frac{A_1}{r_f} = \delta\ddot{r}_f \tag{7}$$

The integration constant A_1 is calculated using the following boundary conditions

$$A_1 \ln R_2 + A_2 = P_b^2 \quad \text{at} \quad r = R_2 \ ,$$

$$A_1 \ln r_f + A_2 = P_f^2 \quad \text{at} \quad r = r_f \tag{8}$$

That leads to

$$\dot{r}_f = -\frac{\sigma}{\delta}\frac{P_b^2 - P_f^2}{T_f r_f \ln\left(r_f / R_2\right)} \tag{9}$$

The function $p_f(r_f)$ in Eq. (9) is unknown and a heat transfer equation needs to be solved to obtain it. The heat conduction equation in cylindrical coordinates is as

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} = 0 \tag{10}$$

The solution is solved as

$$T = B_1 \ln r + B_2 \tag{11}$$

According the Fourier law, the heat flux from the hydration front is

$$q_f = -K\frac{\partial T}{\partial r}\left(r_f\right) = -K\frac{B_1}{r_f} \tag{12}$$

The integration constant B_1 can be calculated using the following boundary conditions

$$K\frac{B_1}{R_1} = h\left(B_1 \ln R_1 + B_2 - T_w\right) \quad \text{at} \quad r = R_1 \ ,$$

$$B_1 \ln r_f + B_2 = T_f \quad \text{at} \quad r = r_f \tag{13}$$

That results in

$$q_f = -\frac{Kh\left(T_f - T_w\right)}{r_f\left[h \ln\left(\frac{r_f}{R_1}\right) + \frac{K}{R_1}\right]} \tag{14}$$

On the same basis, q_f is also determined by the hydration front velocity

$$q_f = -E\dot{r}_f \tag{15}$$

Eqs. (14) and (15) have the same dimension and equalizing with each other leads to

$$\dot{r}_f = -\frac{K}{E}\frac{h\left(T_f - T_w\right)}{r_f\left[h \ln\left(\frac{r_f}{R_1}\right) + \frac{K}{R_1}\right]} \tag{16}$$

The function $T_f(r_f)$ in Eq. (16) is unknown and it is similar to the function $p_f(r_f)$ in Eq. (9). Equalizing Eqs. (9) and (16) determines the function $p_f(T_f)$

$$P_f^2 = P_b^2 - \frac{\delta}{\sigma}\frac{K}{E}T_f \ln\left(\frac{R_2}{r_f}\right)\frac{h\left(T_f - T_w\right)}{\left[h \ln\left(\frac{r_f}{R_1}\right) + \frac{K}{R_1}\right]} \tag{17}$$

At the same time the gas-solid equilibrium follows the Van't Hoff relationship

$$P_f = 10^5 \exp\left(A - \frac{B}{T_f}\right) \tag{18}$$

where A and B are Van't Hoff constants and depend on the hydride material. From Eqs. (17) and (18) the function $T_f(r_f)$ is obtained as

$$10^5 \exp\left(A-\frac{B}{T_f}\right)=\left\{P_b^2-\frac{\delta}{\sigma}\frac{K}{E}T_f \ln\left(\frac{R_2}{r_f}\right)\times\frac{h(T_f-T_w)}{\left[h\ln\left(\frac{r_f}{R_1}\right)+\frac{K}{R_1}\right]}\right\} \tag{19}$$

where K and E are effective thermal conductivity in metal hydride and heat of formation of hydride, respectively. The two equations (16) and (19) are the simplified mathematical model of metal hydride reactor bed.

The present model which describes as above concentrates on the main characteristics of the heat and mass transfer processes in the metal hydride reactor. They indicate the movement of the hydration front, heat transfer and hydrogen filtration. The properties of the hydride materials used in the paper are shown in Table 1 and the thermo-physical properties of materials used in the simulation are shown in Table 2.

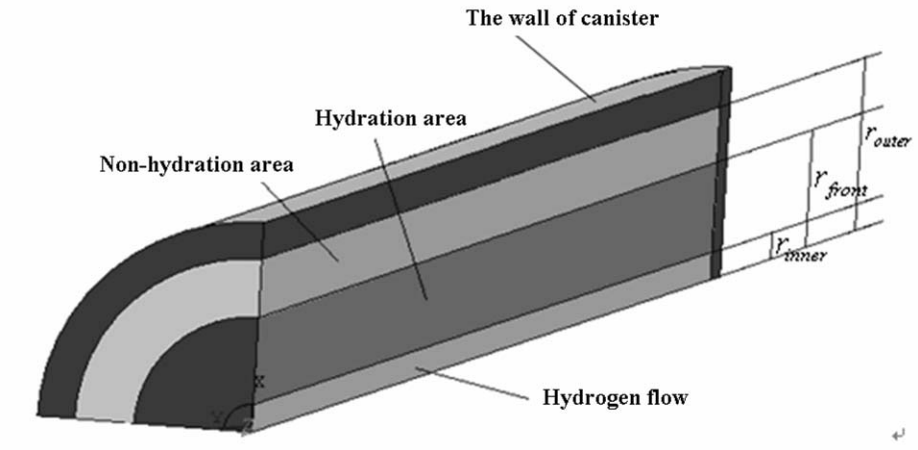


Figure 1. The physical model of metal hydride reactor

Table 1. Properties of hydride materials used in the present analysis

Parameter	**$LaNi_5$**
Molecular weight	432. 4kmole
Heat of hydrogen reaction	30000 kJ mol^{-1} H_2
Specific heat	360 J kg^{-1} K^{-1}
Density	4400 kg m^{-3}
Porosity	0.3
Average diameter	$7.0x10^{-6}$ m
Effective thermal conductivity	0.87 W m^{-1} K^{-1}
Convective heat transfer coefficient	850 W m^{-2} K^{-1}
Hydrogen concentration difference after and before hydration	4.0 katom H $kmol^{-1}$
A for Van't Hoff Eq.	12.94
B for Van't Hoff Eq.	3615

Table 2. Thermal-physical properties of materials

	Thermal conductivity (W m^{-1} K^{-1})	Density (kg m^{-3})	Heat capacity (J kg^{-1} K^{-1})
Stainless outer wall	82	7879	447
Aluminum scroll	237	2702	903
$LaNi_5$	0.87	4400	360

3. Results and discussions

3.1 The design of metal hydride reactor

Metal hydrides have the potential for hydrogen storage and metal hydride reactor provides the space where the materials are filled. Using the metal hydride reactor the large amount of hydrogen can be easily stored and transported. Consequently except the requirements of metal hydride materials in storage capacity and kinetic behavior, the strict demands also put on the reactor design. There are four major concerns of the design of metal hydride reactor, such as enhancement of thermal conductivity of unmodified powder bed, improvement of mass transfer in hydride bed, sufficient space for expansion and good sealing and high bearing pressure.

Metal hydride powder often packed in the reactor to ensure close contact with hydrogen. After the repeating reaction cycles, the powder will shatter into fine particles and then the powder bed has very low thermal conductivity. Temperature needs to be high enough to activate the chemical reactions and low enough to make the hydrogen absorption occur. The low internal heat transfer is often considered as a main problem for practical application. Through the scroll structure and two stage partition design as shown in Figure 2, temperature distribution heterogeneous issues from the hydride formation/ decomposition reaction accompanied with release/uptake of heat can be improved. The parts of the scroll reactor are shown in Figure 3. The hydrogen storage canister comprises a cylindrical metal bed, a void of expansion volume about 25% atop the metal powder and heat transfer enhancement structure (scroll design). Therefore the reactor should own the property of heat exchanger and the design should assure that heat transfer process conducts effectively during reaction.

The scroll fin structure provides the expansion tolerance in radial direction in advance after hydrogen absorption. In addition to preserve enough space for volume expansion, the stress induces from volume expansion in radial direction should release appropriately to prevent from permanent damage. The scroll structure design here can transform volume expansion force into radial direction and eliminate internal elastic stress. The space inside reactor is divided into two stages by the partition design for providing the elasticity of demand when enlarge the system.

The new type scroll reactor which is designed by the Industrial Technology Research Institute (ITRI) is of 30 mm radius and 250 mm height and filled with $LaNi_5$ alloy 1.6 kg. The activation can be conducted under the condition of 12 atm and room temperature. After two hours absorption, the amount of hydrogen storage is 200 Nl under the condition of 8 atm. The hydrogen storage gravimetric capacity is about 1.15 wt% and the reactor was submerged in an isothermal water bath. The water bath temperature is 60^{o}C for hydrogen desorption.

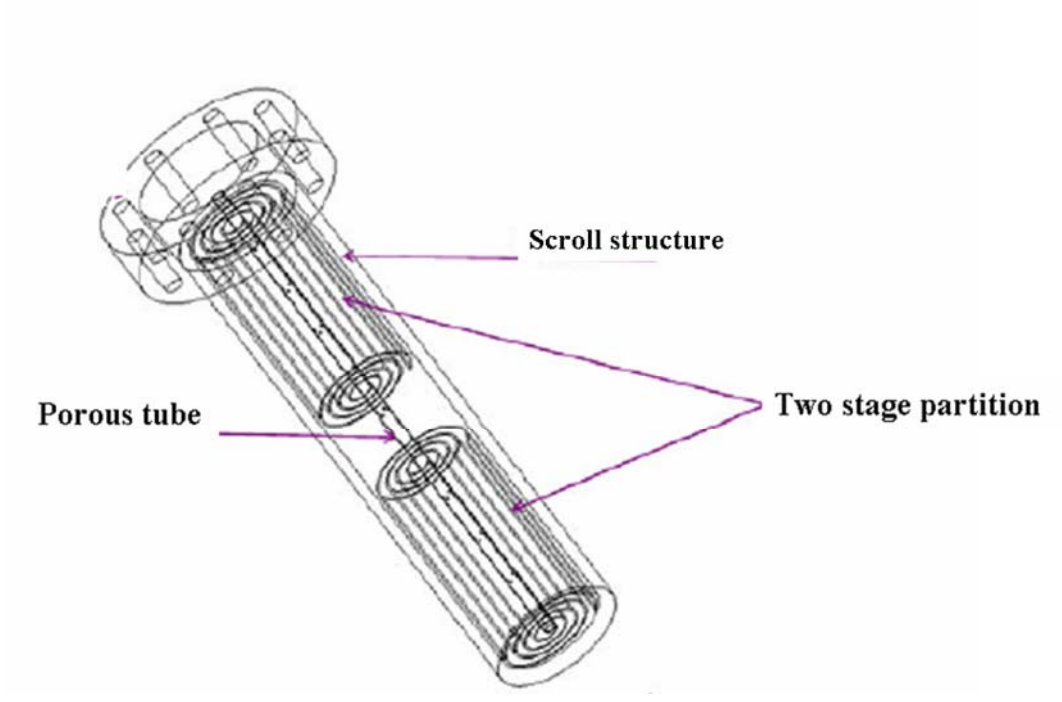


Figure 2. Heat transfer enhancement structure of the designed scroll metal hydride reactor

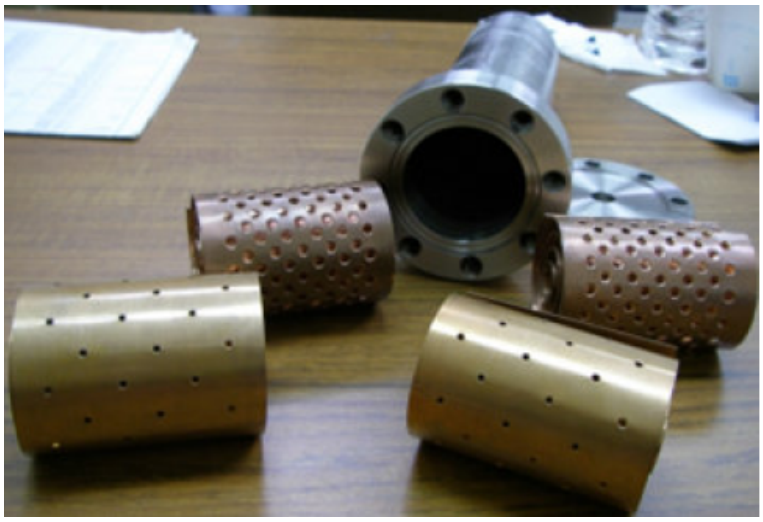


Figure 3. The parts of the scroll reactor

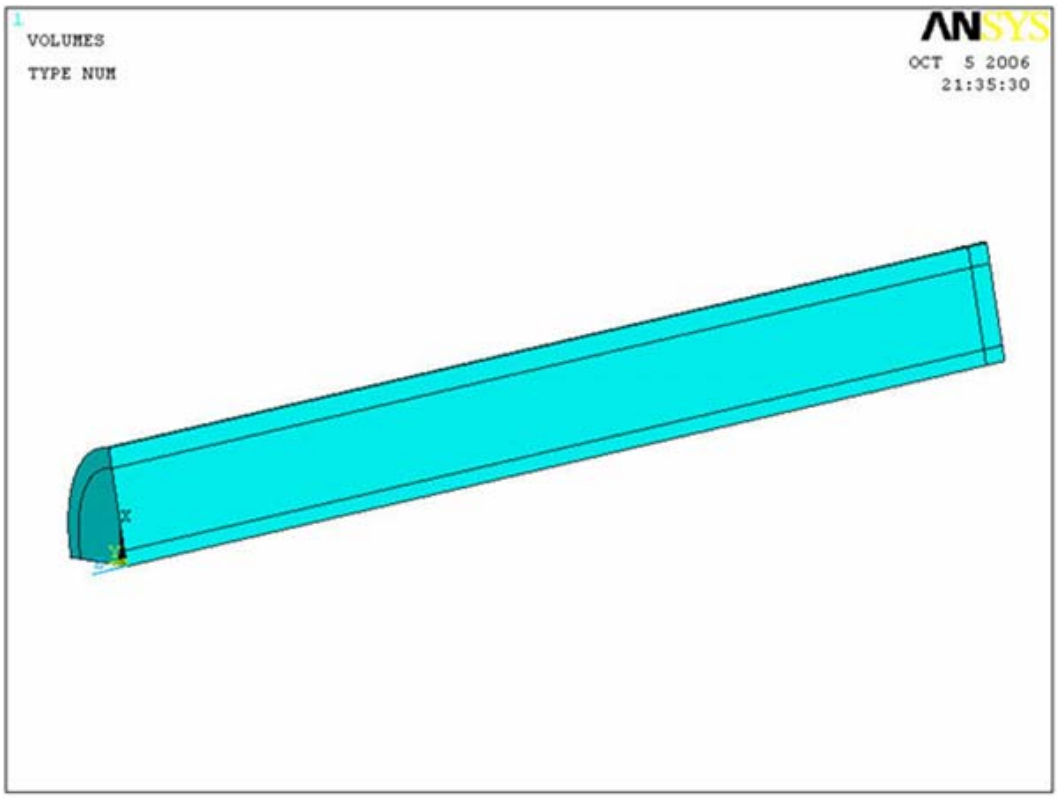
3.2 The simulation results

The simulation here is focus on the heat transfer performance between the origin type and new type scroll structure reactor. The related theory is based on section 2 of the paper. For almost all hydrides, the enthalpy and entropy of hydriding reaction is negative and hydriding reaction is exothermic. The $\triangle H$ is enthalpy change of the hydriding/dehydriding reaction and per mole of hydrogen gas for $LaNi_5$ is about -30.8 kJ. The knowledge of $\triangle H$ is important for the heat management required in practical engineering application. The total volume of hydride material is assumed as 382600 mm^3 in the reactor without heat transfer enhancement mechanism and heat generation rate is assumed as $1.94x10^{-4}$ J mm^{-3} s^{-1} in the following simulations.

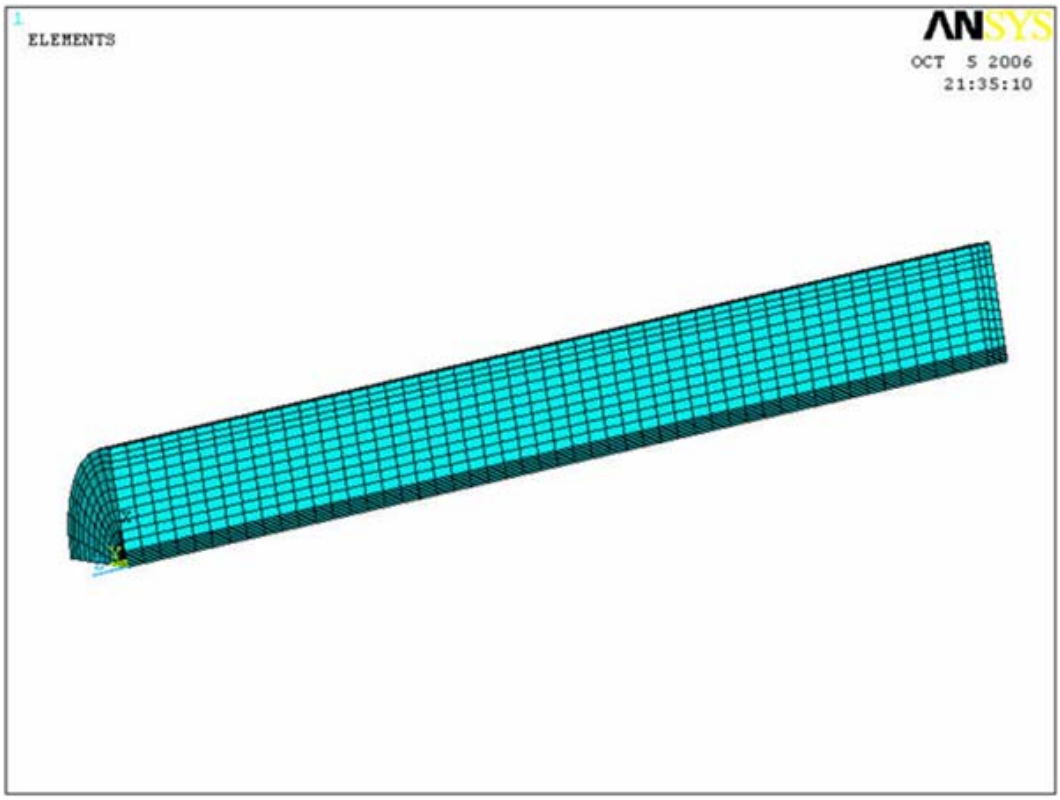
Here the flow issue of hydrogen into reactor by high pressure is ignored and hydrogen absorption by $LaNi_5$ powder uniformly in the reactor is assumed. Heat conduction and convection are considered between different materials and whole simulations are set by hydriding process within 2000 seconds and then there is 16000 seconds for heat dissipation into ambient. There are two different type reactors for comparison, such as original design reactor and scroll design reactor, and the computation models are shown as Figures 4 and 5. The material chosen in outer shell of reactor is stainless and the heat transfer enhancement mechanism of scroll reactor is aluminum. The hydride material is $LaNi_5$ powder of AB_5 group. The convection heat transfer coefficient of outer wall is set by 1650 W m^{-2} K^{-1}.

Figures 4 and 5 show the configuration and grid distribution of the original design reactor and scroll design reactor, respectively. Figures 6 (a and b) are the temperature distribution within the original design reactor after 2000 and 18000 seconds, respectively. Figures 7(a and b) are the temperature distribution within the scroll design reactor after 2000 and 18000 seconds, respectively. The maximum temperature after 2000 seconds evolution is 345.10 K for original design reactor and is 341.97 K for scroll design reactor. The reason of temperature difference between them is the filled volume of $LaNi_5$. The volume of $LaNi_5$ in original design reactor is 382.6 cm^3 and is 303.5 cm^3 in scroll design reactor. The temperature rise depends on the volume of $LaNi_5$ in this period and therefore the temperature inside reactor is higher in the origin design reactor than in the scroll design reactor. The following next 16000 seconds heat dissipation period totally depends on the effect of with or without the heat transfer enhancement mechanism. The maximum temperature after 18000 seconds is 344.18 K for original design reactor and is 330.95 K for scroll design reactor. The heat transfer enhancement mechanism makes heat dissipation effectively and reduces the temperature inside reactor up to 11 K.

Using a porous tube located in the center of tank to direct the hydrogen into the reactor can improve the hydriding/dehydriding kinetic behavior. Although it sacrifices a part of refilled space, it can improve the hysteresis phenomenon. Figures 8 and 9 illustrate the temperature distribution without and with porous directed tube design after 100 seconds, respectively. It reveals that the depth of hydride reaction can penetrate to the bottom of the reactor in Figure 9. The radial direction diffusion of hydride reaction also occurs at the same time. Compared with the Figure 8, the penetration depth of hydride reaction is only half of the reactor and the kinetic behavior is worse than the case in Figure 9.

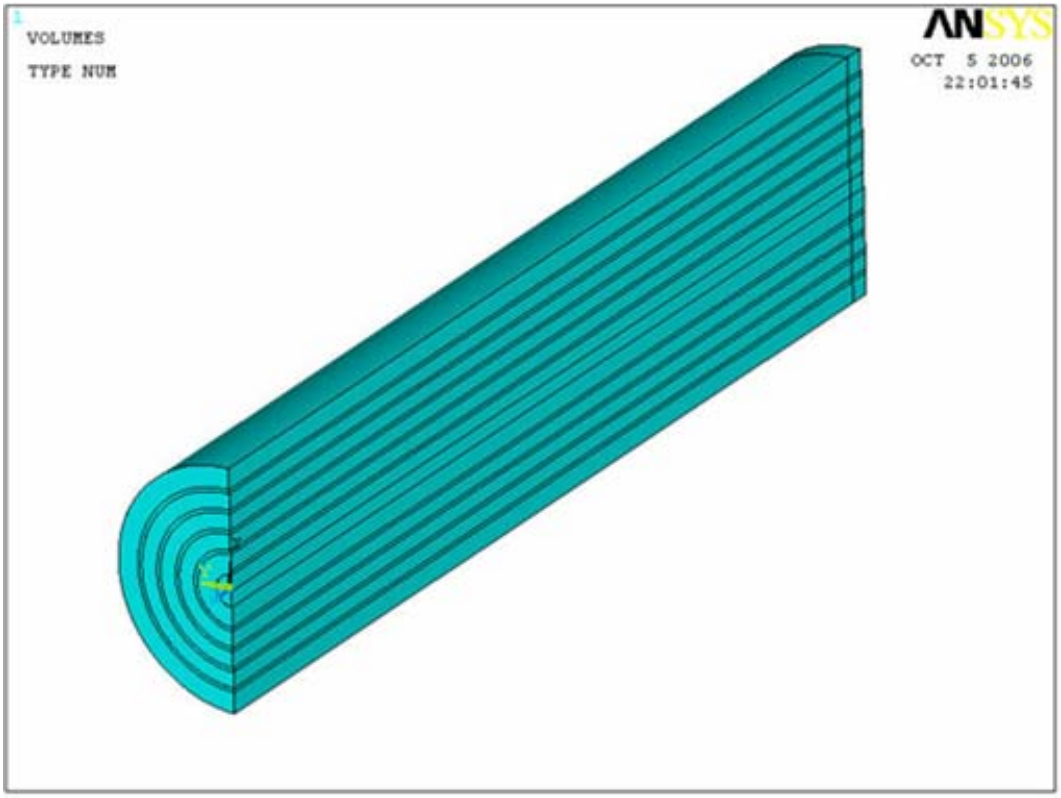


(a)



(b)

Figure 4. (a) Configuration of the original design reactor; and (b) Schematic showing grid distribution within the original design reactor



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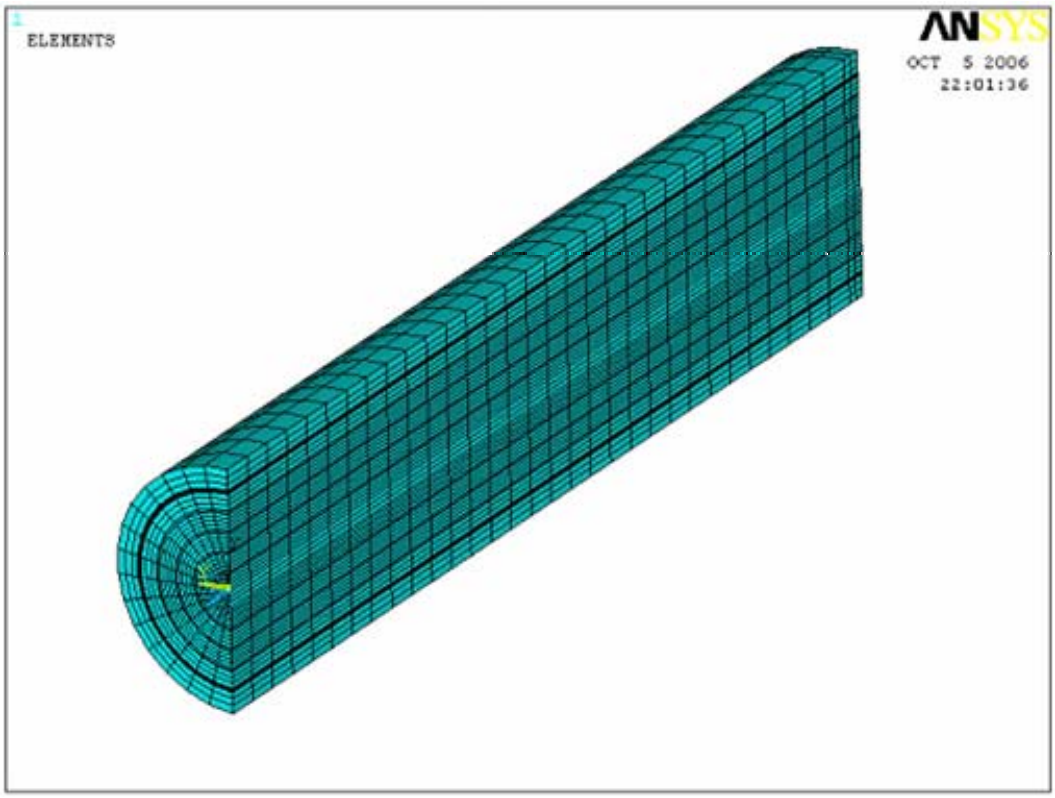
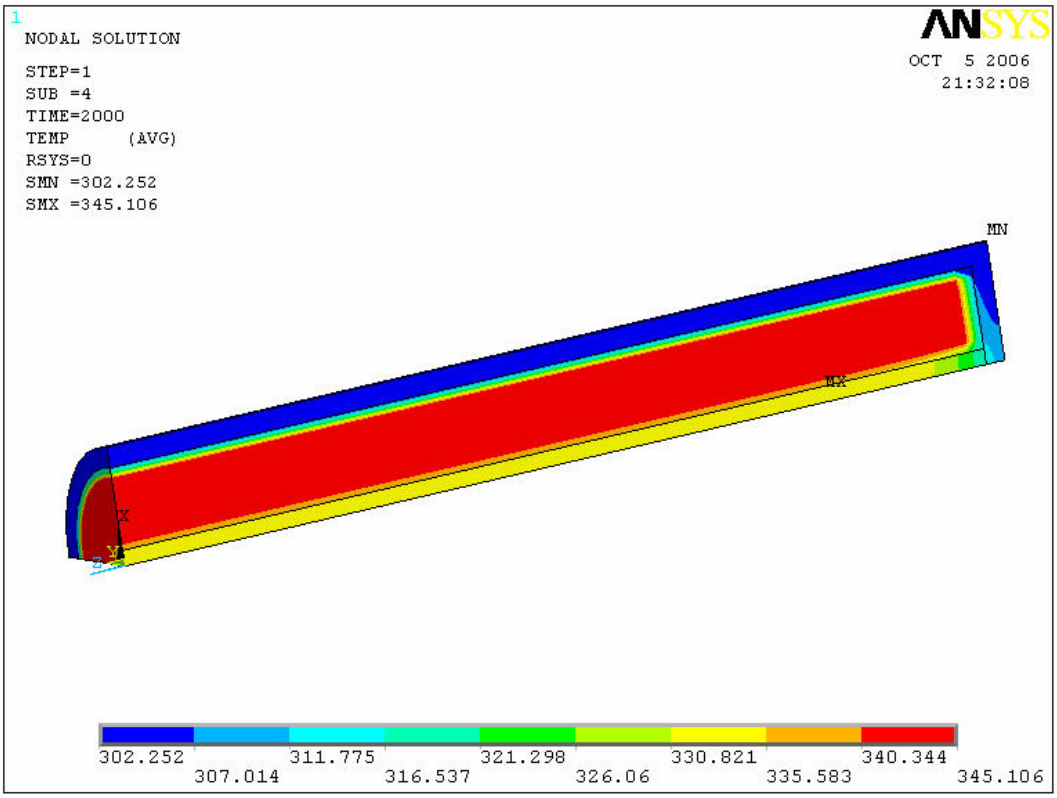
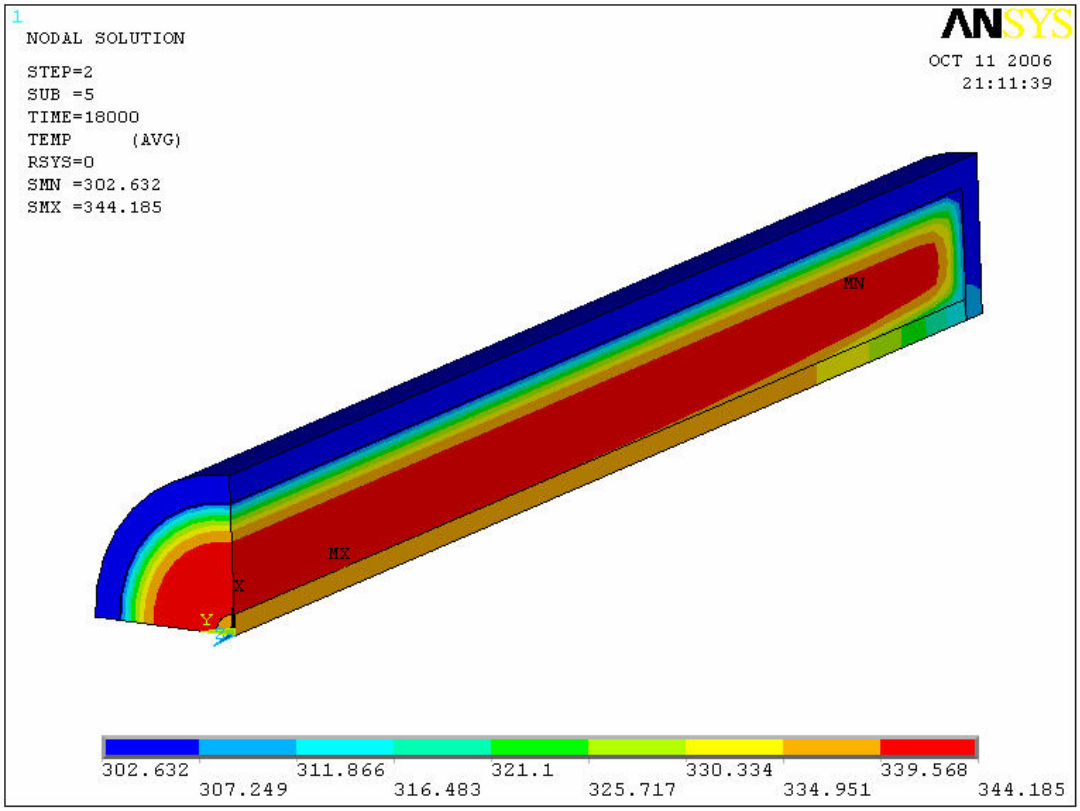


(b)

Figure 5. (a) Configuration of the scroll design reactor; and (b) Schematic showing grid distribution within the scroll design reactor

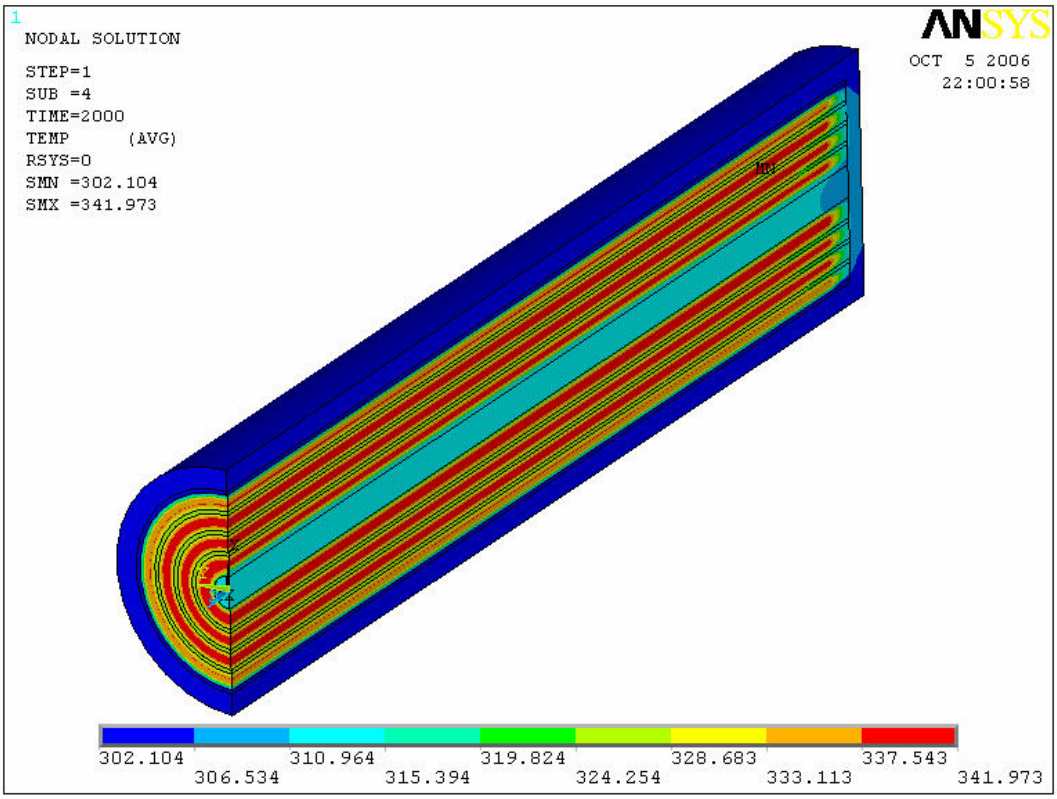


(a)

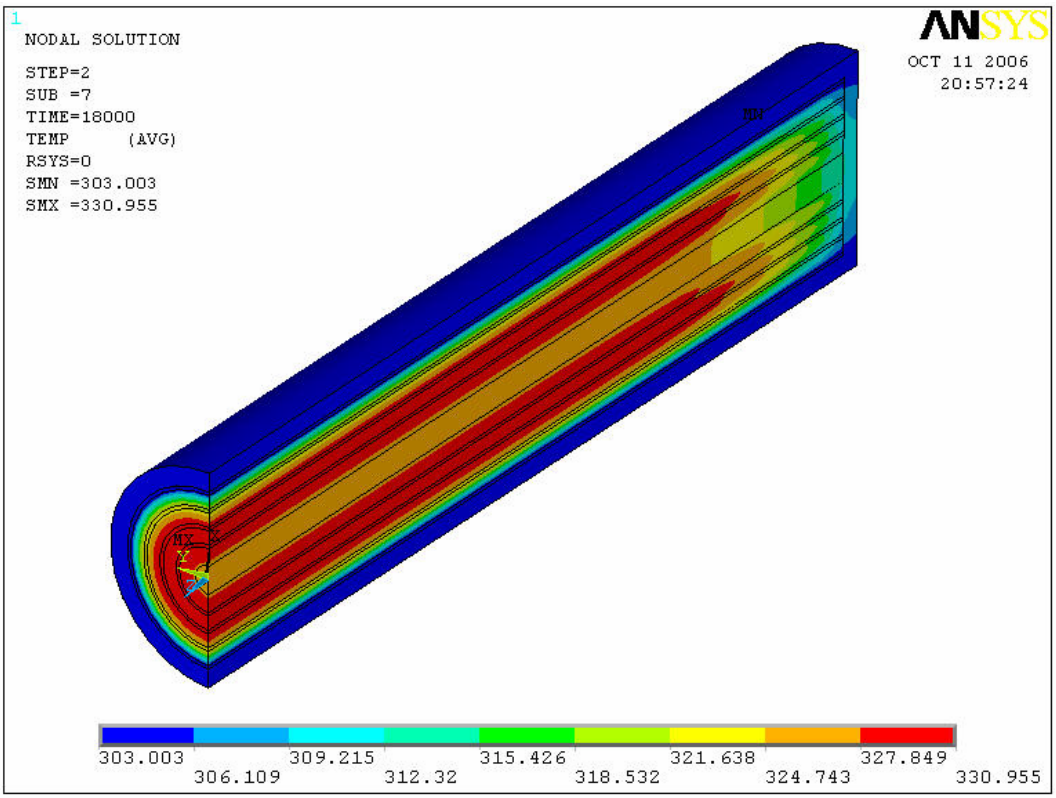


(b)

Figure 6. (a) Temperature distribution within the original design reactor after 2000 seconds; and (b) Temperature distribution within the original design reactor after 18000 seconds



(a)



(b)

Figure 7. (a) Temperature distribution within the scroll design reactor after 2000 seconds; and (b) Temperature distribution within the scroll design reactor after 18000 seconds

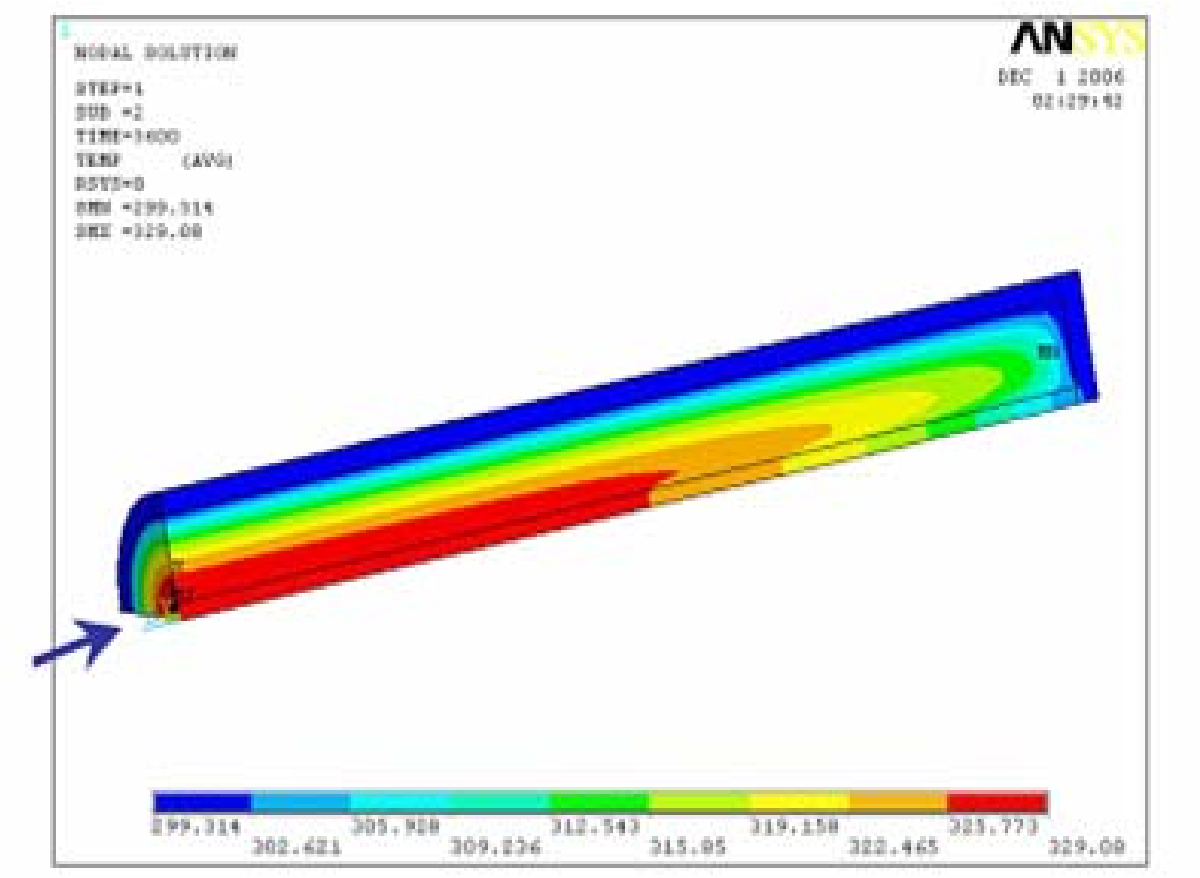


Figure 8. Temperature distribution without porous directed tube after 100 seconds

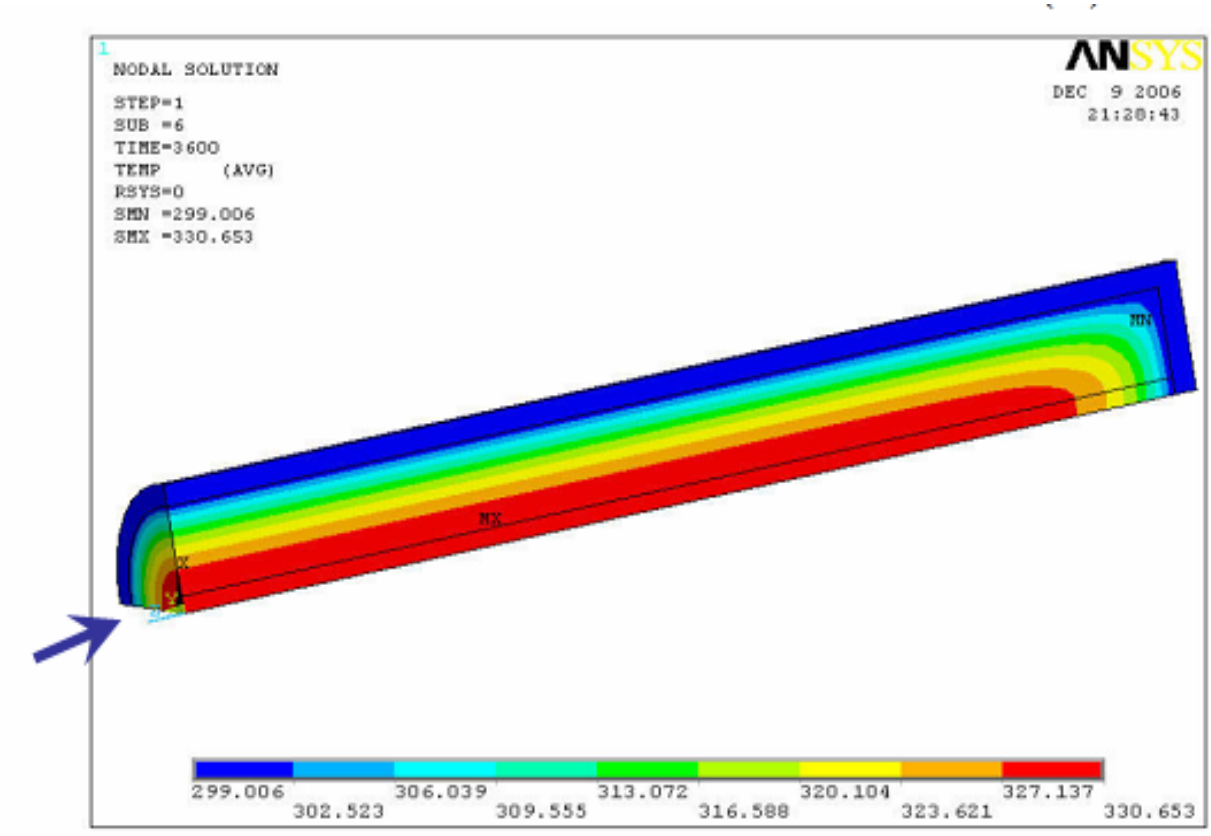


Figure 9. Temperature distribution with porous directed tube after 100 seconds

4. Conclusion

The performance of our new design reactor is comparable to the product in the market. Through the simulation results, the scroll design can improve the temperature distribution in the reactor. The reactor's hydrogen absorption limit is dependent on the cooling temperature and the simulation results reveal that heat transfer enhancement can improve kinetic behavior. It also approved that the porous tube for directing hydrogen can increase the penetration depth of hydride reaction and decrease the hydrogen absorption time.

Nomenclature

K	Permeability of porous medium	r	radial direction
M	Molecular weight	T	Temperature
$\dot{m}$	mass of hydrogen absorption rate	t	time
P	Pressure	u_r	radial component of the gas velocity
$\tilde{R}$	Universal gas constant	u_z	axial component of the gas velocity

Greek symbols

ε	porosity	ρ_s	density of solid
ρ_g	density of gas	μ_g	Molecular viscosity of hydrogen

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