Hydrogen absorption from gas mixture in a metal-hydride reactor: mathematical model and numerical results

V.I. Artemov, G.G. Yankov, D.O. Lazarev

Moscow Power Engineering Institute, Russia

Presented by

Lazarev D.O.

General assumptions

- The differential equations of heterogeneous medium written in the multispeed continuum model terms are used as main equations of mathematical model.
- Gaseous phase is homogeneous mixture of *N* components, one of which is hydrogen.
- Solid phase includes impermeable structures (unit walls), permeable "passive" structures (internal tube with porous wall), permeable "active" structures (layers of intermetallic particles).
- The gaseous phase is ideal from the thermodynamic viewpoint; specific isobaric heat capacity of gas mixture components is constant; the viscous dissipation and compression work are negligible.

Mass balance

- The mass conservation equation of solid is:

$$(1-\varepsilon)\rho_s^0 \frac{\partial X}{\partial t} = \frac{M_{\mathrm{Me}}}{M_{\mathrm{H}}} \dot{m};$$

- the mass conservation equation of *k*-th mixture component is:

$$\frac{\partial}{\partial t}\left(\varepsilon \rho_g x_k\right) + \nabla \cdot (\varepsilon \rho_g \vec{\mathbf{w}} x_k - \rho_g D_k^* \nabla x_k) = -\dot{m} x_k;$$

- the equation to calculate an absorption rate is (Jemni et.al.):

$$\dot{m} = F_a \rho_s^0 \frac{M_{\mathrm{H}}}{M_{\mathrm{Me}}} (X_{\max} - X), \quad F_a = C_a \exp\left(-\frac{T_a}{T_s}\right) \ln\left(\frac{p_{\mathrm{H}_2}}{p_{eq}}\right).$$

Momentum equation

- i-projection ($i = r, \theta, z$):

$$\frac{\partial}{\partial t}\left(\varepsilon\rho_g w_i\right) + \nabla\cdot\left(\varepsilon\rho_g \vec{\mathbf{w}} w_i - \varepsilon\mu_g \overrightarrow{\nabla w_i}\right) = -\varepsilon(\overrightarrow{\nabla p})_i - \varepsilon\frac{\mu_g}{k_i} w_i,$$

- permeability k_i is given by:

$$k_i = C_k \bar{d}_p^{\,2}\left(\frac{\varepsilon}{1-\varepsilon}\right)^2, \quad C_k = 2.37\times 10^{-3}.$$

It should be noted that a pressure gradient in gaseous phase due to hydraulic resistance does not affect the absorption under the inlet pressure $p_0 \sim 1$ MPa. Our previous works showed that use of different equations for permeability does not significantly affect the hydrogen absorption rate.

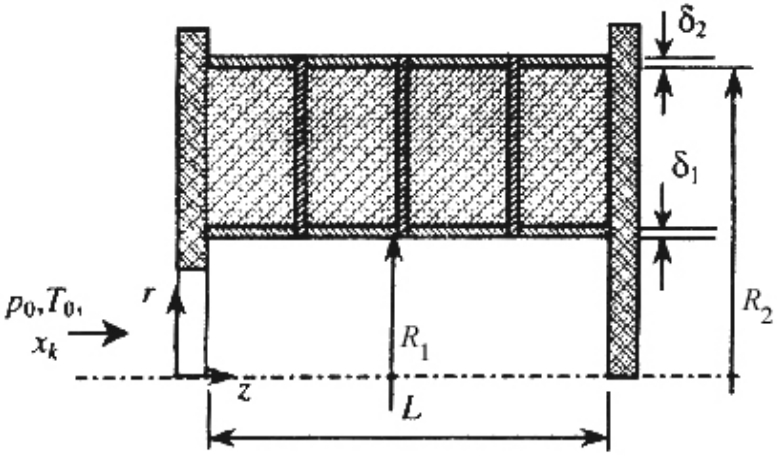
Energy equations

- For the solid: $(1-\varepsilon)\rho_s^0 c_{p,s}\frac{\partial T_s}{\partial t} = \nabla\cdot\left(\lambda_s^*\nabla T_s\right) + \alpha_{gs}\left(\frac{F}{V}\right)(T_g - T_s) + \dot{m}\Delta H;$
- For the gas: $\frac{\partial}{\partial t}\left(\varepsilon\rho_g c_{p,g}T_g\right) + \nabla\cdot(\varepsilon\rho_g \mathbf{w} c_{p,g}T_g + \vec{q}_g) = \alpha_{gs}\left(\frac{F}{V}\right)(T_s - T_g) - \dot{m}c_{p,\mathrm{H}_2}T_{gs}.$
- The heat transfer coefficient is given by Ranz's equation $\mathrm{Nu} = 2 + 1{,}1\,\mathrm{Pr}^{1/3}(\mathrm{Re}_d\,\varepsilon)^{0,6}.$

In order to determine the sensitivity of computational results to heat transfer coefficient the calculations were made for Nusselt number value, given by (6), and values, which were three orders less and greater than the first one respectively: $\mathrm{Nu}_{min} = 2\cdot10^{-3}$, $\mathrm{Nu}_{max} = 2\cdot10^{3}$. However the temporal evolution of absorbed hydrogen concentration was almost the same in all three cases. Besides the temperatures of gaseous and solid phases were equal for all three **Nu** values mentioned above. Thus the assumption of local thermal equilibrium can be applied for the analysis of the given metal hydride reactor. This result is rather evident under developed interface, i.e. when ratio of interface area to the volume of dispersed medium is great enough

$$\left(\frac{F}{V} = \frac{6(1-\varepsilon)}{\bar{d}_p} \sim 10^6\,\frac{1}{\mathrm{m}}\right).$$

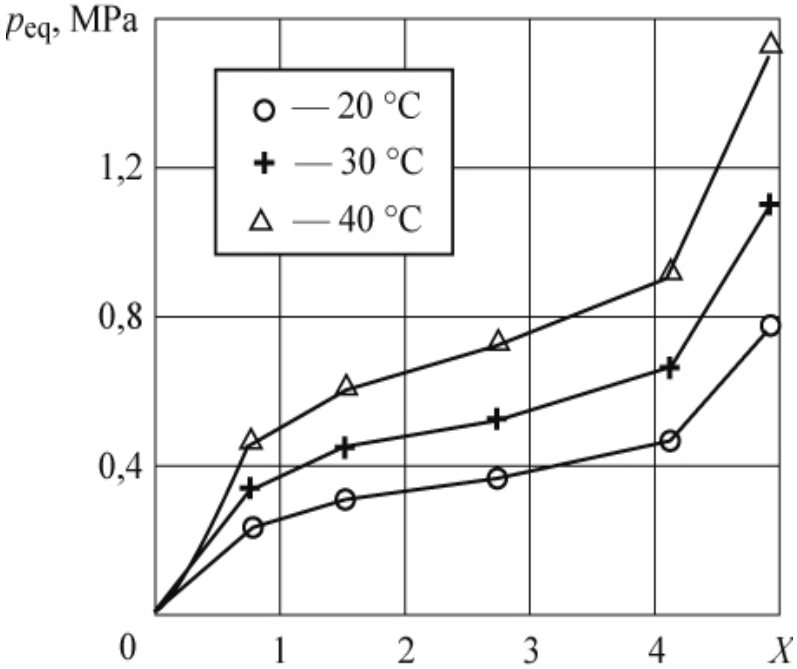
Reactor design (1st embodiment)



Schematic sketch
of the metal hydrogen reactor

Inlet pressure	p_0 = 0.8, Mpa
Inlet gas temperature	T_0 = 20 °C
Heat transfer coefficient	α_f = 2000,W/(m²K)
Temperature of cooling fluid	T_f = 15 °C
Reactor length	L = 1100 mm
Thickness of external tube wall	δ_2 = 1 mm
Diameter of external tube	$D = 2\times R_2$ = 110 mm
Thickness of porous tube wall	$d = 2\times R_1$ = 90 mm
Mean particle diameter	$\bar{d}_p = 2\times 10^{-3}$ mm
Porosity	ε = 0.43

Properties of the absorbent



Experimental absorption pressure—composition isotherms of $M_{0.8}La_{0.2}Ni_{4.1}Fe_{0.8}Al_{0.1}$

Thermodynamical properties of the $M_{0.8}La_{0.2}Ni_{4.1}Fe_{0.8}Al_{0.1}$

ΔH, *kJ/mole* H_2	29 ± 0.8
ΔS, *J/(K·mole* H_2*)*	107 ± 3
ρ_s^0, g/cm^3	7.76
Plateau hydrogen composition, %	0.2 – 1.2

Initial and boundary conditions

- The inlet gas temperature $T_0 = 20$ ºC, the inlet pressure $p_0 = 0.8$ MPa, the mole concentrations of components in supply gas mixture are $\tilde{x}_{N_2} : \tilde{x}_{CO_2} : \tilde{x}_{H_2} = 1,5\% : 1,9\% : 96,6\%$.

- The temperature of cooling fluid at the external surface of unit walls $T_f = 15$ ºC, the heat-transfer coefficient $\alpha_f = 2000$ W/(m^2×K).

- The initial mass concentration of bound hydrogen $x_{HS} = 2\times10^{-3}$, initial hydrogen-to-metal atomic ratio $X = 0.84$, the mass concentration hydrogen-to-metal atomic ratio are connected by relationship $x_{HS} = \dfrac{M_H X}{M_{Me} + M_H X}$. Initial temperature $T_g = T_s = 20$ ºC.

Additional correlations of the model

- Effective thermal conductivity: an evaluation technique

$$\lambda'_{gk} = \frac{\lambda_{gk}}{1 + 2Kn_k \dfrac{2-a}{a}}, \qquad \bar{\lambda}'_{gk} = \int_0^\infty \lambda'_{gk}(r_\text{п}) f_0(r_\text{п}) dr_\text{п},$$

$$\lambda_g = \sum_k \frac{\bar{\lambda}'_{gk}}{1 + 1{,}065\left(\sum\limits_{m \neq k} G_{km} \dfrac{\tilde{x}_m}{\tilde{x}_k}\right)}, \qquad G_{km} = \frac{\left(1 + \sqrt{\dfrac{\mu_k}{\mu_m}} \sqrt[4]{\dfrac{M_m}{M_k}}\right)^2}{2^{3/2} \sqrt{1 + \dfrac{M_k}{M_m}}},$$

$$\lambda_e = \frac{\lambda_g}{\varepsilon^3}.$$

Additional correlations of the model

- Effective thermal conductivities of gas and solid

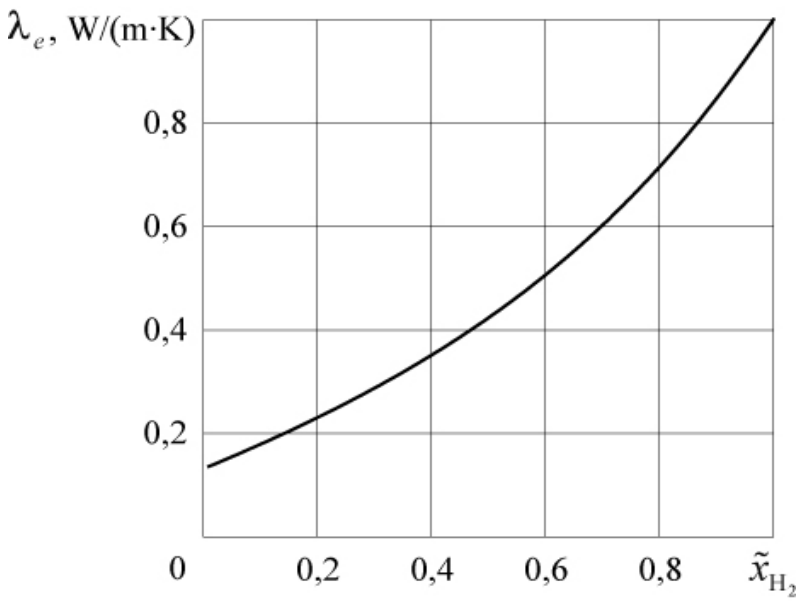
Effective thermal conductivity of solid phase λ_s^* is assumed to be equal 0.1 W/(m×K) in porous region. In fact this value is an upper bound for the λ_s^*. Such low value of effective thermal conductivity of solid phase in porous region is due to high contact resistance between metal hydride particles in the porous bed. Experimental study of effective thermal conductivity in evacuated beds (Hahne E.,Kallweit J.) shows that for pressures below 100 Pa the effective thermal conductivity drops sharply and its value is in the region 0.004—0.01 W/(m×K).

Effective thermal conductivity of gaseous phase is given by

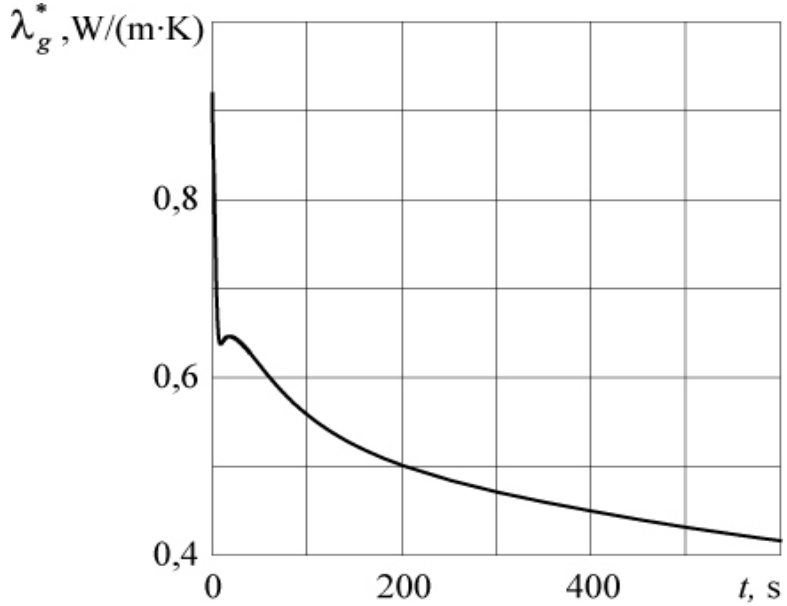
$$\lambda_g^* = \lambda_e - \lambda_s^*;$$

$$\vec{q}_g = -\lambda_g^* \nabla T.$$

Additional correlations of the model



Effective thermal conductivity versus mole hydrogen concentration



Temporal evolution of the effective thermal conductivity in one of the central control volumes

Hydrogen sorption under presence of gas admixtures

High rate of hydrogen absorption and great heat effect of reaction result in admixtures concentrating in the reactor during a short period of time in the beginning of the process. As a result hydrogen absorption rate is limited by hydrogen diffusion.

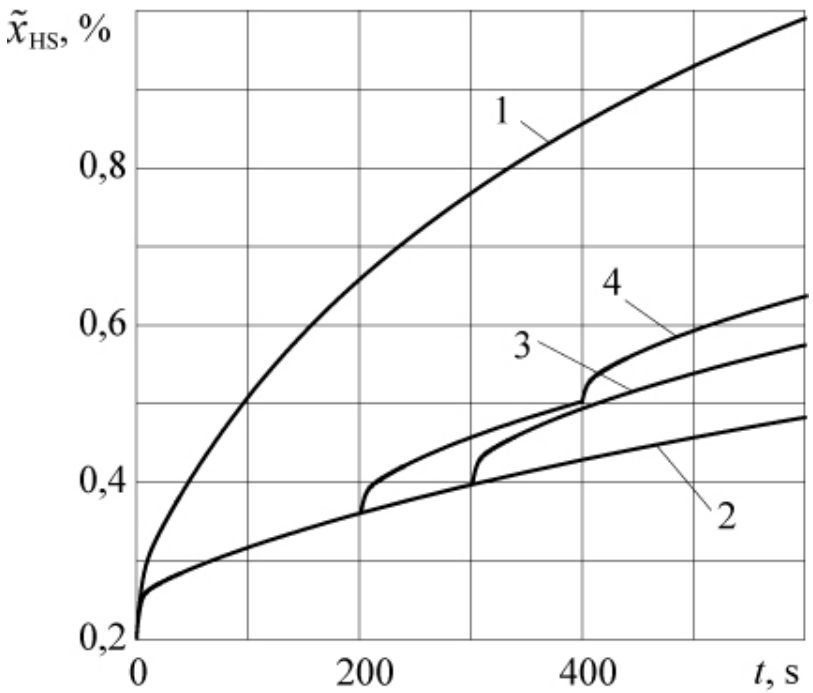
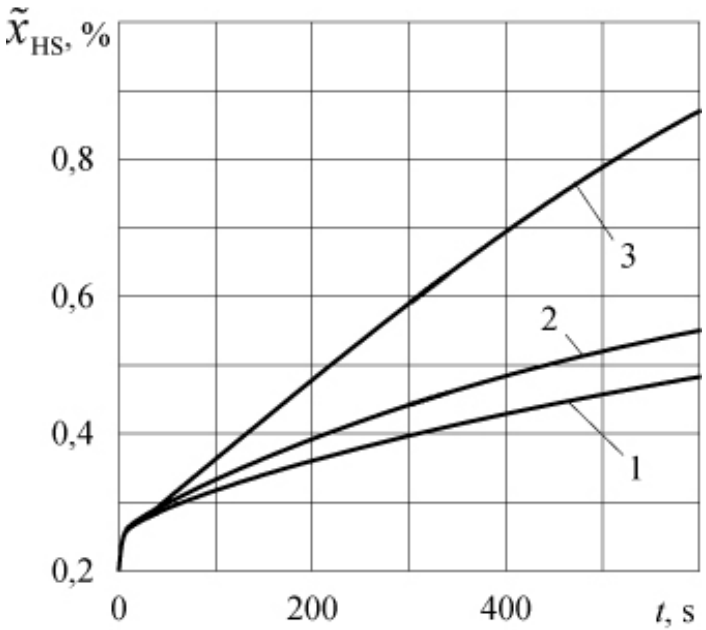


Figure shows temporal evaluation of hydrogen absorbed. Curve *1* represents absorption of pure hydrogen. Curve *2* represents the gas mixture. The presence of admixtures significantly decreases efficiency of metal hydride equipment, That is why it is necessary to remove admixture from the reactor. The operation of admixtures removing is denoted as PSA-like absorption mode. Curves *3* and *4* in the figure represent a reactor charging in PSA-like absorption modes. In the first mode (curve *3*) expulsion is carried out every 300 s, in the second one (curve *4*) — every 200 s. The figure shows that expulsion considerably increases the efficiency of the metal hydride reactor charging.

Hydrogen sorption under presence of gas admixtures



Temporal evolution of absorbed hydrogen mole concentration:
1 — with natural convection has not been take into account; *2* — the inlet is directed upward; *3* — the inlet is directed downward

Analysis of calculation results shows that heavy admixtures move from the ballast volume of the reactor to the supply pipeline under the influence of gravity force if the reactor inlet is directed downward. Thus self-purification of the unit is carried out and the hydrogen concentration in the ballast volume is nearly equal to its initial value. The mole concentration of the absorbed hydrogen after 600 s of charging tends to the value corresponding to absorption of pure hydrogen. If the reactor inlet is directed upward the natural convection effect is less considerable. The increase in concentration of absorbed hydrogen is result from hydrogen concentration leveling in the ballast volume induced by natural convection. A concentration leveling means that admixtures are distributed in the ballast volume uniformly and do not accumulate in the places where absorption is most intensive.

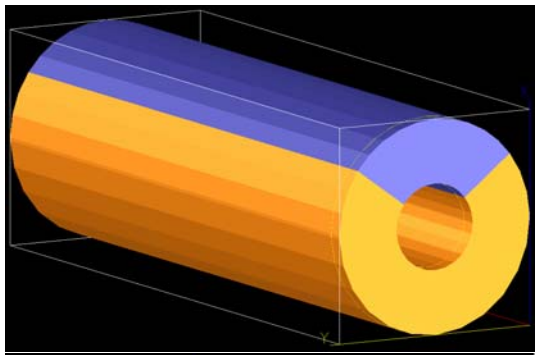
It should be noted that boundary conditions at the inlet of the metal hydride reactor simulate the situation when supply pipeline connects the reactor with a vessel with a certain volume. The volume of the vessel should be great enough to assume the proportion of the gas mixture to be constant. Thereupon the data shown in figure represents the highest possible self-purification efficiency due to natural convection effect. Certainly this model possibly differs from the real conditions greatly, but it allows to give a demonstration of the influence of natural convection upon the processes in the reactor.

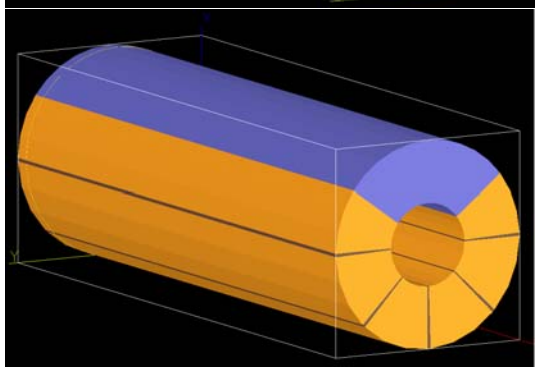
Problem of heat removal

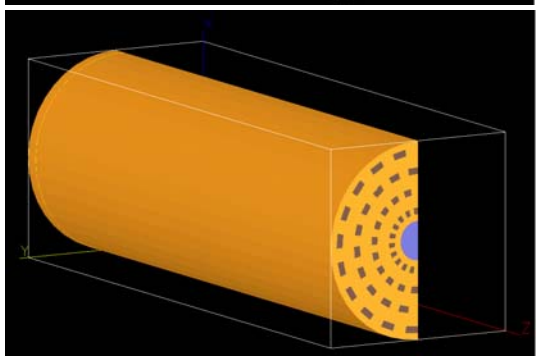
The present study shows that the presence of nonabsorbable admixtures changes the hydrogen absorption kinetics in metal hydride devices fundamentally and results in slump in efficiency of these devices. Rapid accumulating of gas admixtures in the porous bed and in the ballast volume of the metal hydride reactor prohibits from supply the hydrogen to the absorbing intermetallic alloy and leads to the increase in accumulator charge time. Utilization of PSA-like absorption mode allows to solve the problem and to increase efficiency of metal hydride devices by reducing characteristic charge time.

Low effective thermal conductivity is another factor, which substantially limits hydrogen absorption process. It was shown that the value of effective thermal conductivity is not exceeding 1. Low-intensity of heat removal from the heat-generating zone of the reactor results in fast warming up of the reactor and decrease in hydrogen absorption rate. Additional measures for intensification of heat removal should be taken to increase the efficiency of the device. Three different design embodiments are analyzed. High emphasis is placed on providing of effective reactor cooling.

Problem of heat removal







Second embodiment of reactor design represents cylindrical chamber partially filled with absorbent. The intermetallic alloy in the form of fine powder is packed between internal and external cylindrical walls. Internal cylindrical wall is permeable for gas, and hydrogen passes to the reactor through end opening and internal permeable wall.

External wall radius – 50 mm, internal wall radius – 20 mm,

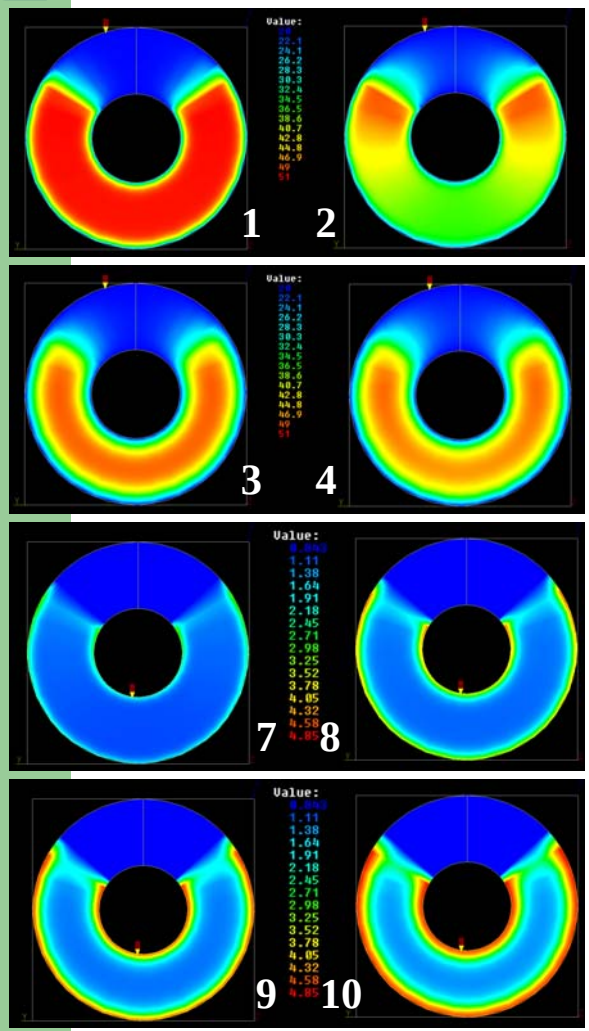
reactor length – 300 mm.

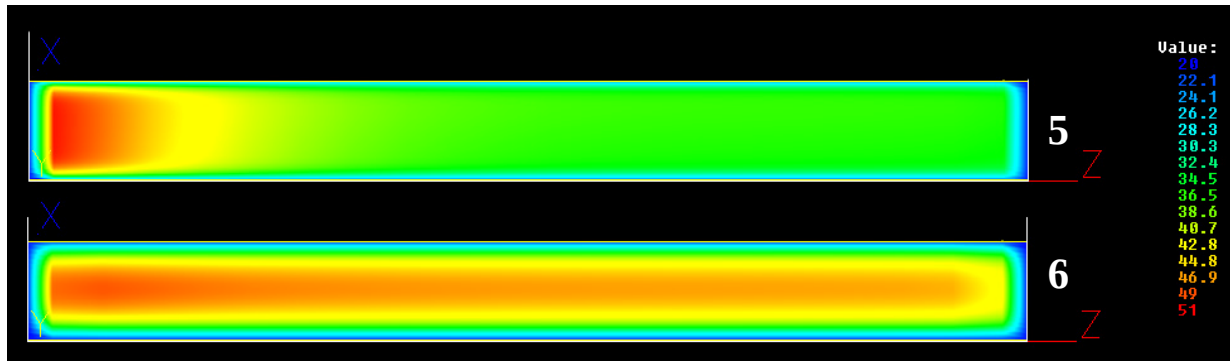
Other reactor parameters as well as initial and boundary conditions are identical to the first embodiment of the reactor design.

In third embodiment four thin porous fins are placed in the reactor chamber. The fins connect internal and external walls of the chamber.

In fourth embodiment a tube matrix is placed in the reactor chamber. The matrix consists of water-cooled tubes of small diameter. Absorbent fills tube space. Internal wall radius is 10 mm.

2nd embodiment of MeH reactor design





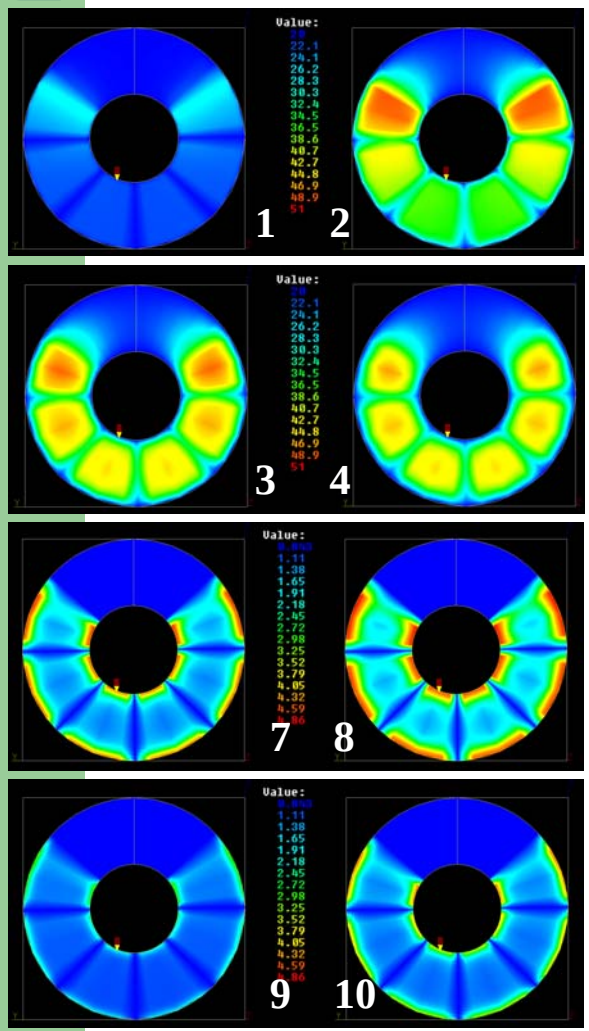
Field of gas temperature:

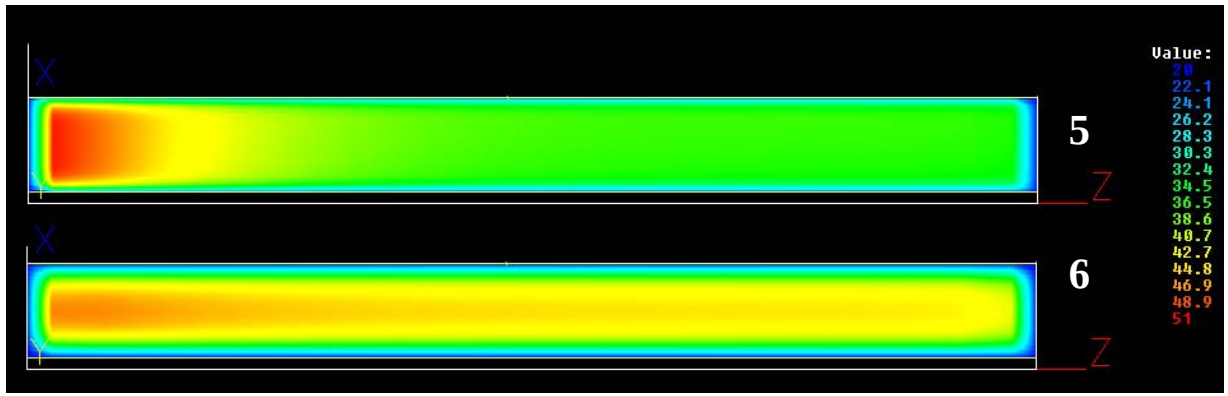
1 — at the inlet cross-section after 50 s; *2* — at the central cross-section after 50 s; *3* — at the inlet cross-section after 600 s; *4* — at the central cross-section after 600 s; *5* — at longitudinal section ($\varphi = \pi$) after 50 s; *6* — at longitudinal section ($\varphi = \pi$) after 600 s.

Field of hydride concentration at central cross-section of the reactor:

7 — after 10 s; *8* — after 50 s; *9* — after 300 s; *10* — after 600 s.

3rd embodiment of MeH reactor design





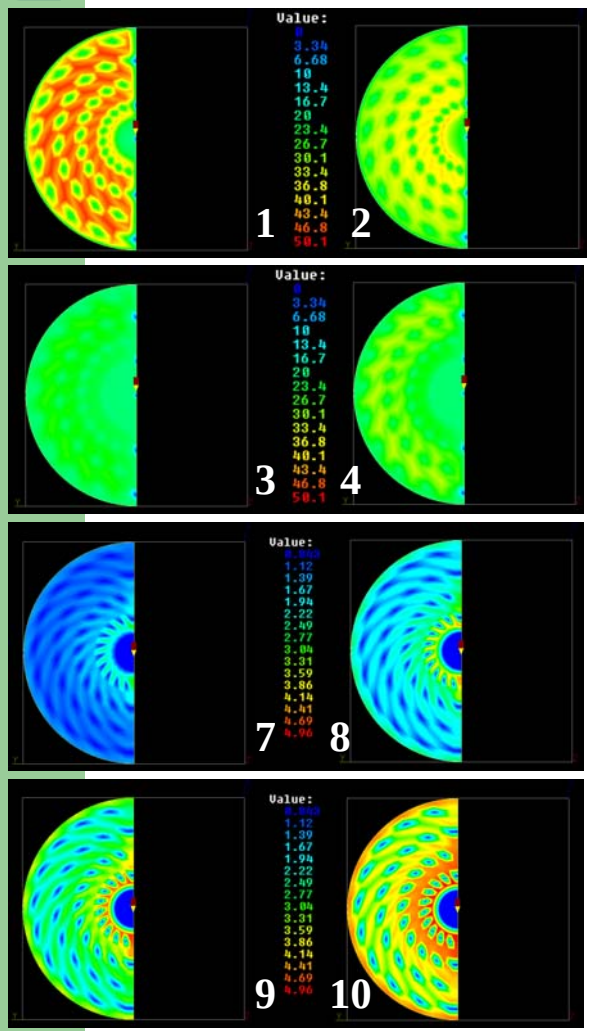
Field of gas temperature at the central cross-section:

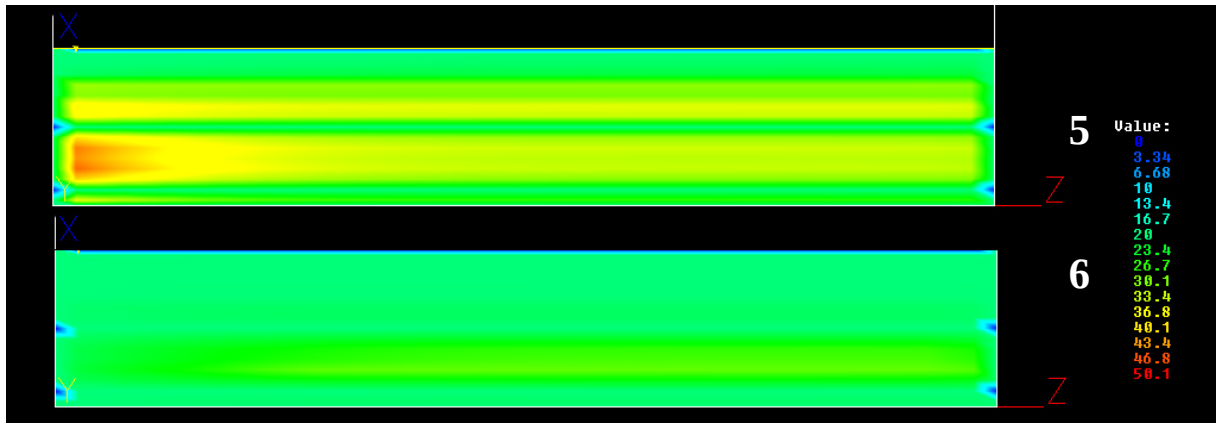
1 —after 1 s; *2* — after 50 s; *3* — after 300 s; *4* — after 600 s; *5* — at longitudinal section ($\varphi = \pi$) after 50 s; *6* — at longitudinal section ($\varphi = \pi$) after 600 s.

Field of hydride concentration at central cross-section of the reactor:

7 — after 50 s; *8* — after 150 s; *9* — after 300 s; *10* — after 600 s.

4th embodiment of MeH reactor design





Field of gas temperature:

1 — at the inlet cross-section after 50 s; *2* — at the central cross-section after 50 s; *3* — at the inlet cross-section after 600 s; *4* — at the central cross-section after 600 s; *5* — at longitudinal section ($\varphi = \pi$) after 50 s; *6* — at longitudinal section ($\varphi = \pi$) after 600 s.

Field of hydride concentration at central cross-section of the reactor:

7 — after 10 s; *8* — after 50 s; *9* — after 300 s; *10* — after 600 s.

Embodiment effectiveness comparison

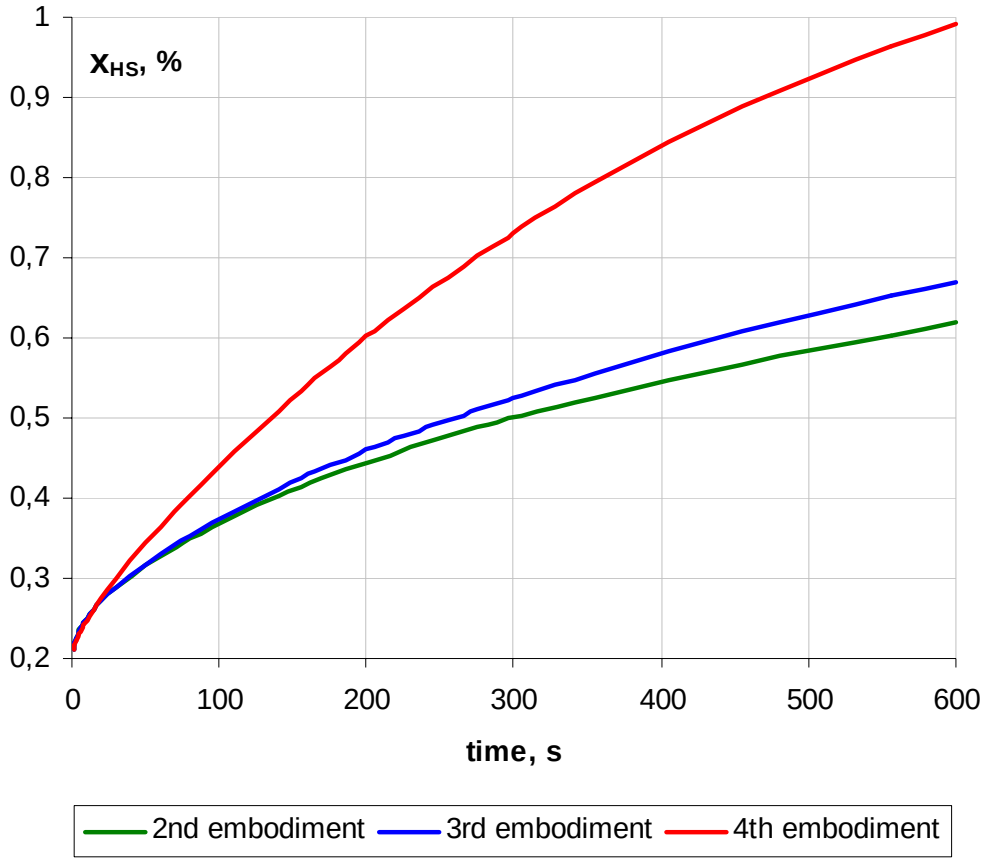


Figure shows temporal evolution of absorbed hydrogen mole concentration for 2nd, 3rd and 4th embodiments of the reactor design.

Use of the fins results in increase of absorbed hydrogen concentration on 8% at charging time of 10 min. Use of tube matrix for porous bed cooling results in increase of absorbed hydrogen concentration on 40% at charging time of 10 min. Thus the 4th embodiment of the hydrogen accumulator design seems to be most optimal it terms of thermal effectiveness.

Conclusions

- Multipurpose software implementing three dimensional mathematical model which allows to analyze heat and mass transfer in metal hydride devices is developed.
- The mathematical model takes into account the presence of passive admixtures in hydrogen.
- It was shown that gas admixtures slow down heat and mass transfer in the reactor.
- The low effective thermal conductivity is the second main factor which limits the hydrogen absorption rate in metal hydride reactor.
- Effective heat elimination from the absorption zone is the main engineering problem to solve in order to design a effective hydrogen accumulator.

Acknowledgments

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