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# Simulation of Hydrogen Absorption in a Magnesium Hydride Tank

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**Abstract:** This paper summarizes the outcomes of a numerical study about the phenomenon of hydrogen absorption in an axisymmetric tank geometry containing magnesium hydride heated to 300°C and at moderate storage pressure 1 MPa. The governing equations are solved with a fully implicit finite volume numerical scheme (as implemented in the commercial software FLUENT). Different kinetic reaction equations modeling hydrogen absorption are considered and the related numerical simulations are compared with experimental results. Spatial and temporal profiles of temperature and concentration in hydride bed are plotted.

**Keywords:** Hydrogen storage, Magnesium hydrides, CFD simulation, Absorption kinetic equation.

## Nomenclature

| | |
|---|---|
| $Cp$ | specific heat, J/kg.$K^{-1}$ |
| $C_a$ | kinetic coefficient , $s^{-1}$ |
| $\Delta H$ | molar enthalpy of reaction at standard conditions, J/mol |
| $K$ | permeability, $m^2$ |
| $P$ | hydrogen pressure, Pa |
| $P_{eq}\,(T)$ | equilibrium pressure, Pa |
| $R$ | universal gas constant = 8.314 J/mol.K |
| $S$ | source term of reaction, mol/m.s |
| $\Delta S$ | molar entropy of reaction at standard conditions, J/mol.K |
| $wt$ | maximum weight percentage of hydrogen in the material, % |

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### Greek symbols

| | |
|---|---|
| $\alpha$ | absorption rate |
| $\lambda$ | thermal conductivity, W/m.K |
| $\varepsilon$ | porosity |
| $\rho$ | density, kg/m$^3$ |
| $d\alpha/dt$ | hydriding velocity, s $^{-1}$ |

### Subscripts and superscripts

| | |
|---|---|
| *e* | energy |
| *eff* | effective |
| *eq* | balance |
| *g* | gas |
| *H* | hydrogen |
| *M* | metal |
| *m* | mass |
| *MH* | metal hydride |
| *i* | initial |

## 1 Introduction

Because of the huge amounts of dangerous gases emitted by industry, the predicted shortage of fossil fuels and the announced general climate change, SOFC fuel cells running with hydrogen could be the solution to the recurring problem of intermittent renewable energy. These kinds of systems are particularly interesting for electricity production in isolated areas, for the daily stabilization of electricity demand or as security high power kits. However, the major obstacle to the rapid growth of this technology is the hydrogen storage in the most compact volume. One of the most promising methods is that of storing hydrogen in metal hydrides. Indeed, magnesium hydride is a very good substance for reversible hydrogen storage because of its highest capacity of storage (7.6 %m.$H_2$) compared to the others such as $TiVCrH_6$ (2 %m.$H_2$), $FeTiH_{1,95}$ (1.6 %m.$H_2$), $LaNi_5H_{6,7}$ (1.5 %m.$H_2$). Its volume capacity (111 kg/m$^3$) is greater than that of liquid hydrogen (71 kg/m$^3$), that's why it would be used in a large scale in the few next years. The hydrogen storage in a solid form offers significant advantages, like reducing the tank dimensions, resulting chemical reactions running at moderate temperatures 300°C and at pressures about 1 to 1 MPa; also, hydrogen density in the solid form is more important than the one in molecular form. Finally, this type of storage allows better safety compared to conventional methods such as compression or liquefaction of hydrogen.

Many experimental and computational studies were realized in order to improve the hydrogen tank performances. M. H. Mintz and Y. Zeiri (1994) studied the effects on the corresponding reaction mechanism and intrinsic kinetic parameters of the MH powder particle size distributions, its particle shape variations and its time distributions from the beginning of hydrogen absorption reaction. They realized the corresponding equations which models the hydriding mechanism and the intrinsic kinetic parameters. A. Jemni and S. Ben Nasrallah (1995) realized one of the first numerical studies of 2D - hydrogen reactor. The results showed the importance of the geometry, inlet pressure and inlet temperature choice. Y. Kaplan et al. (2004) presented a mathematical model for hydrogen storage in a metal hydride bed; the team concluded that a rapid charge needs efficient cooling. G. Barkhordarian's team (2004) investigated the effect of $Nb_2O_5$ concentration on the kinetics of the magnesium hydrogen reaction at 300°C and 250°C. Their results show that the activation energy decreases exponentially with catalyst additions, reaching the lower saturation limit and that there is a change in the rate-limiting step with catalyst content. P. Muthukumar et al. (2007) made a parametric investigation of a metal hydride hydrogen storage device, they showed that overall increasing heat transfer coefficient is not beneficial. A. Phate et al. (2007) carried out a computational analysis of a cylindrical metal hydride bed; their conclusion is that the concentration gradient in the bed is the major driving force of hydrogen flow in the bed. Marty et al. (2008) added an experimental validation to the computational simulations of the hydrogen storage tank with metal hydrides; their goal was to obtain performances according to the objectives imposed by a stationary cogeneration system. Askri et al. (2009) made a numerical investigation of heat and mass transfer of a 3D annular tank. Results showed that the use of fins enhances heat transfer and consequently 40% improvement of the time required for 90% storage can be achieved over the case without fins. Y. Zheng et al. (2010) investigated the effect of coolant flow and the variation of inlet pressure of hydrogen on temperature profiles of hydriding and dehydriding. The conclusion of their study was that by varying the coolant flow rates, a hydrogen filling time of 12 min has been achieved. A CFD model for simulating hydrogen storage in an activated carbon tank was described by R. Chahine et al. (2012); this model showed that the amount of absorbed hydrogen is greater than that of the compressed gas hydrogen.

Because of these many coupled phenomena, numerical simulation allows us to anticipate and understand the evolution of the hydrogen storage reaction. In addition, the numerical tool will save considerable time for the optimization of hydrogen tank design. FLUENT was used to perform numerical simulations. One of the advantages of this software consists of the important part devoted to the modeling of thermodynamics and kinetics reaction between a gas and a porous medium. A file called (UDF: User Defined Function) in C grouping models was included in the calculations. The purpose of this work is to find the best reaction kinetics equation modeling the phenomenon of hydrogen absorption.

## 2 Geometry and mathematical formulation

The tank geometry consists of a domain with (L = 450 mm) × (H = 7.5 mm) dimensions. It is surrounded by an aluminum shell which equalizes the temperature. Also, it is cooled by a process which ensures effective further reactions. Hydrogen enters from a lateral left side. The activated magnesium hydride porous powder (Metal alloy) is retained on the other side by a thin filter. The right side wall is considered adiabatic.

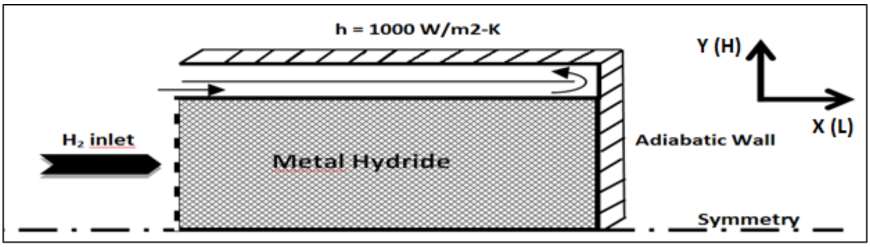


Figure 1: Schematic of a basic tank.

In order to simplify the model, some assumptions are adopted. First, hydrogen is considered as an ideal gas between the hydride pores and its generated flow before the absorption phase is negligible. Then, the hydrogen temperature is locally the same as that of the powder, the flow is laminar between the powder grains, the radiative transfer in the porous medium is neglected, the pressure and friction energies are negligible, the inlet temperature is constant. Finally, the resolution method used is the finite volume in a two-dimensional, axisymmetric, laminar regime and at unsteady flow.

The governing equations of the phenomenon are:

### 2.1 The equations of mass balance and Darcy

- Continuity equation in the gas phase

$$\varepsilon_M \cdot \frac{\partial \rho_g}{\partial t} + \mathrm{div}\left(\rho_g \cdot \vec{U}\right) = -S_m \cdot M_{H2}$$

- Continuity equation in the solid phase

Mass transfer is taken into account by Fluent with the continuity equation and the Darcy one:

$$\varepsilon_{MH} \cdot \frac{\partial \rho_{MH}}{\partial t} = S_m \cdot M_{H2} \qquad (1)$$

The term source of hydrogen mass depends on the reaction rate and can be expressed:

$$S_m = \rho_{MH} \cdot wt \cdot (1 - \varepsilon) \cdot \frac{d\alpha}{dt} \qquad (2)$$

The Darcy equation is: $\overrightarrow{\nabla} P_{H2} = -\frac{\mu}{K} \cdot \overrightarrow{U}$

This expression is the balance between viscous friction and pressure gradient where (K) is the permeability of the metal hydride. Considering a high porosity of the material and a low velocity of the flow, we can suppose that: $\overrightarrow{\nabla} P_{H2} = 0$.

## 2.2 The energy equation

The energy conservation equation simplified and solved by fluent in both phases is:

$$\varepsilon \cdot \rho_g \cdot C_{p_g} \cdot \frac{\partial T}{\partial t} + (1-\varepsilon) \cdot \rho_s \cdot C_{p_s} \cdot \frac{\partial T}{\partial t} + \varepsilon \cdot \rho_g \cdot C_{p_g} \cdot \nabla \left( T \cdot \overrightarrow{U} \right) = \nabla(\lambda_{eff} \nabla T_{MH}) + S_e \qquad (3)$$

- Since the solid medium (s) + gas (g) is treated as a continuous medium with:

$$\rho_{MH} \cdot C_{p_{MH}} = \varepsilon \cdot \rho_g \cdot C_{p_g} + (1-\varepsilon) \cdot \rho_m \cdot C_{p_m} = \int_i \varepsilon_i \cdot \rho_i \cdot Cp_i$$

and $\lambda_{eff} = \varepsilon \cdot \lambda_g + (1-\varepsilon) \cdot \lambda_m$

So, to the absorption source term of the energy equation taken into account through a module in Fluent UDF is:

$$S_e = \frac{\triangle H}{M_{H2}} \cdot S_m \qquad (4)$$

The material thermal parameters are a function of the powder compactness, temperature and hydrogen inlet pressure and absorption rate. Also, a good knowledge of the thermal conductivity of the activated powder is particularly necessary to obtain perfect simulation accuracy. This value was already obtained experimentally and taken into account such as: $\lambda_{eff}$ = 0.48 W/m/K.

## *2.3 Initial and boundary conditions*

### *2.3.1 Initial conditions*

Initially, the powder temperature, the gas pressure and the hydride density of the reaction bed are considered uniform through the tank and the system was assumed under the P-c-T equilibrium.

$$T_s = T_{H2} = T_i; \quad P_{H2} = P_i; \rho_{H2} = \rho_i$$

### *2.3.2 The boundary conditions*

The boundary conditions taken into consideration are:

- Hydrogen is supplied axially to the hydride bed through a porous filter.

$$\left.\frac{\partial \mathrm{T_{H2}}}{\partial \mathrm{X}}\right|_{\mathrm{x=0}} = 0; \quad \left.\frac{\partial \mathrm{P_g}}{\partial \mathrm{X}}\right|_{\mathrm{x=0}} = 0$$

- Wall with heat transfer at the top of tank (forced convection by cold fluid)

$$-\lambda_{\mathrm{eff}} \left.\frac{\partial \mathrm{T_{MH}}}{\partial \mathrm{Y}}\right|_{\mathrm{y=H}} = \mathrm{h} \cdot (\mathrm{T_{MH}} - \mathrm{T_\infty}); \quad \left.\frac{\partial \mathrm{P_g}}{\partial \mathrm{Y}}\right|_{\mathrm{y=H}} = 0$$

- Adiabatic right tank wall:

$$\left.\frac{\partial \mathrm{T_{MH}}}{\partial \mathrm{X}}\right|_{\mathrm{x=L}} = 0, \quad \left.\frac{\partial \mathrm{P_{H2}}}{\partial \mathrm{X}}\right|_{\mathrm{x=L}} = 0$$

## *2.4 Modeling of thermodynamics and kinetic reaction*

The modeling of thermodynamics and kinetics reaction permits the calculation of the spatial and temporal evolution of absorption rate and hydriding velocity into the material. These laws are included in the UDF that allows an iterative calculation at the end of each time step ($\Delta$t).

There are different mechanisms that can model the reaction kinetics. In this study, we have compared the results of these models in order to know the best mechanism which closely approximates the results obtained from the experiences of the real phenomenon. The considered mechanisms are:

with: $\mathrm{k(T,P)} = \mathrm{C_a} \cdot \mathrm{e}^{\frac{-\mathrm{E_a}}{\mathrm{RT}}} \cdot \frac{\mathrm{P} - \mathrm{P_{eq}}}{\mathrm{P_{eq}}}$ (the Arrhenius law) and $\mathrm{E}_a$ , $\mathrm{C}_a$ , R are extracted values from the experiment study [Chaise, Marty, de Rango and Fruchart (2009)]. The terms of the absorption rate ($0 < \alpha < 1$) and the hydriding velocity $\frac{d\alpha}{dt}$ are derived from the models equations of different reaction.

Table 1: Different modeling mechanisms equations [R. Varin's book (2009)].

| Models Equation | Method |
|---|---|
| $k.t = \alpha$ | Chemisorption |
| $k.t = [- \ln (1-\alpha)]^{1/2}$ | 2D / Johnson-Mehl-Avrami-Kolmogorov : two-dimensional growth of existing nuclei with constant interface velocity (JMAK-2D) |
| $k.t = 1-\ln(1-\alpha)^{1/3}$ | 3D / Contracting Volume with constant interface velocity (C V-3D) |
| $k.t = 1-\ln(1-\alpha)^{1/2}$ | 2D / Contraction Volume with constant interface velocity (C V-2D) |

The law which defines the thermodynamic equilibrium pressure ($P_{eq}$) between the two domains of existence of Mg and $MgH_2$ is the Van't Hoff law. It is given by the following expression:

$$P_{eq}(T) = P^{\circ} \cdot e^{\left[\frac{\triangle H}{RT} - \frac{\triangle S}{R}\right]} \tag{5}$$

where : $P^{\circ} = P_{atm}$, ΔH : the absorption enthalpy, ΔS: the entropy of the reaction.

## 3 Validation

Our results were compared with the published experimental data. In fact, we performed FLUENT simulations and confronted them with those available in relevant studies such as [Askri, Ben Salah, Jemni and Ben Nasrallah (2008)]. Figure 2 shows the profile of the average temperature of the metal hydride bed as a function of elapsed hydrogen absorption time. The figures 3 and 4 present the comparison with the average bed temperature contours and the hydrogen capacity with the contribution of [Muthukumar and V. Ramana (2008)]. Our computational results showed good agreement with those available in the literature.

This study aims to model the heat transfer and reaction kinetics during hydrogen loading magnesium hydride tank. FLUENT industrial software was chosen to model this problem. It uses the finite volume method to discretize the equations of the mathematical model. Then, it solves in an unsteady case the equations of mass, momentum and energy and includes the kinetic reaction differential equations with the appropriate physical parameters. These physical parameters used in the numerical simulations are presented in Tab. 2.

## 4 Results and Discussion

Computations were carried out under windows with an Intel core i5 processor. The simulations were executed on several grids and time steps ranging from 0.01s to 1s.

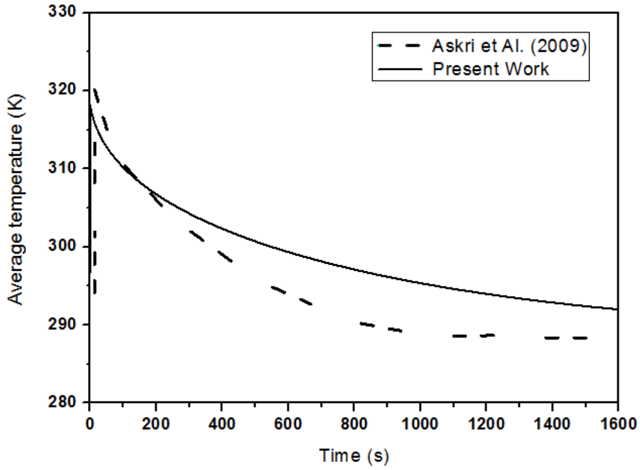


Figure 2: Absorption average bed temperature profiles with $P_{H2}$= 3 MPa and Δt = 0.1s.

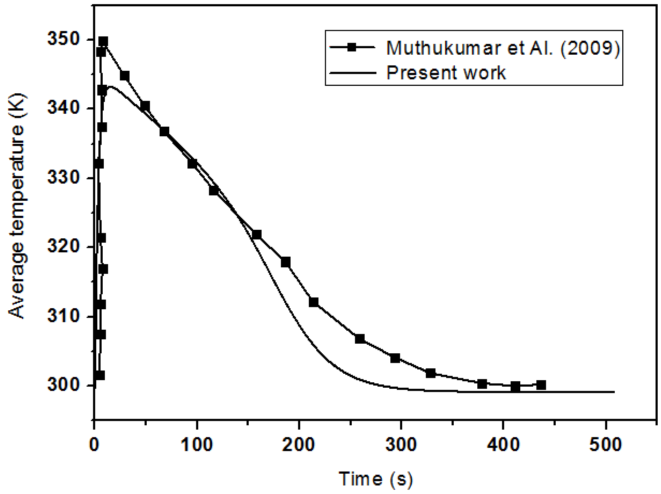


Figure 3: Absorption average bed temperature profiles with $P_{H2}$ = 2 MPa and Δt = 0.1s.

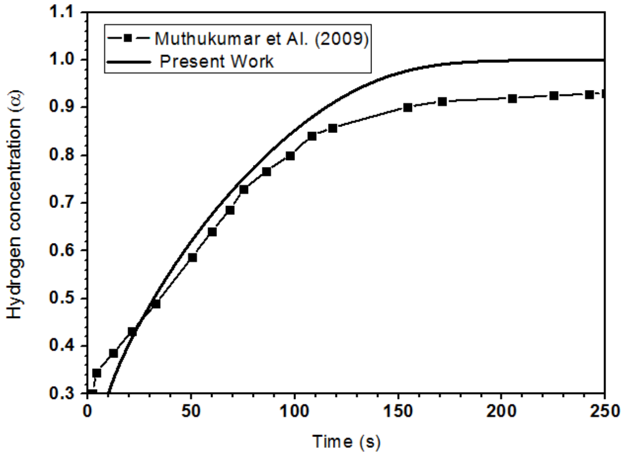
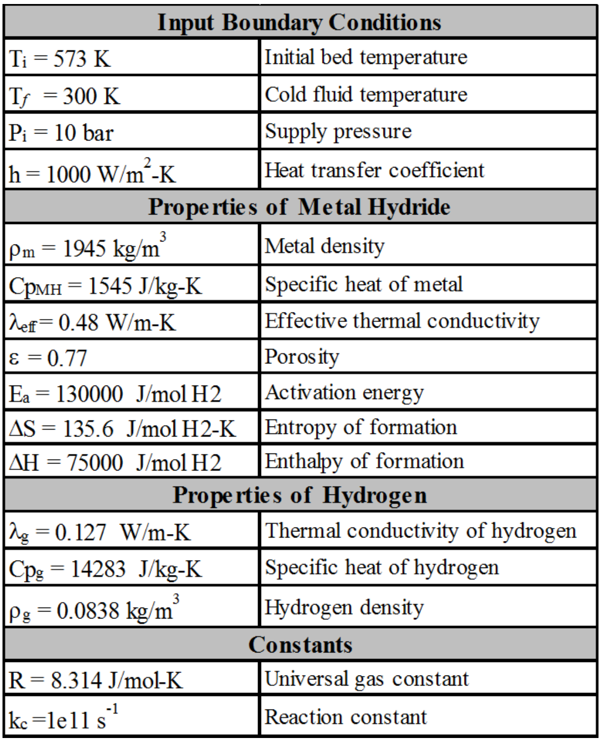


Figure 4: Variation of hydrogen concentration with time.

Table 2: Main parameter values used in computations [A. Chaise's thesis (2008)]



| **Input Boundary Conditions** | |
|---|---|
| $T_i = 573$ K | Initial bed temperature |
| $T_f = 300$ K | Cold fluid temperature |
| $P_i = 10$ bar | Supply pressure |
| $h = 1000$ W/m$^2$-K | Heat transfer coefficient |
| **Properties of Metal Hydride** | |
| $\rho_m = 1945$ kg/m$^3$ | Metal density |
| $Cp_{MH} = 1545$ J/kg-K | Specific heat of metal |
| $\lambda_{eff} = 0.48$ W/m-K | Effective thermal conductivity |
| $\varepsilon = 0.77$ | Porosity |
| $E_a = 130000$ J/mol H2 | Activation energy |
| $\Delta S = 135.6$ J/mol H2-K | Entropy of formation |
| $\Delta H = 75000$ J/mol H2 | Enthalpy of formation |
| **Properties of Hydrogen** | |
| $\lambda_g = 0.127$ W/m-K | Thermal conductivity of hydrogen |
| $Cp_g = 14283$ J/kg-K | Specific heat of hydrogen |
| $\rho_g = 0.0838$ kg/m$^3$ | Hydrogen density |
| **Constants** | |
| $R = 8.314$ J/mol-K | Universal gas constant |
| $k_c = 1e11$ s$^{-1}$ | Reaction constant |

The mesh corresponding to 396 × 210 nodes and time step. $\Delta t = 10^{-2}$ s was therefore adopted for all numerical simulations, in order to optimize the calculating time and the convergence criterion. At the end of the computations, we observed (fig.5) that the hydrogen absorption phenomenon which starts with preheated discharged tank from 573 K at supply pressure of 10 MPa causes increase in the metal hydride temperature during the first ten seconds of loading and reaches different maximum temperatures from 625 K to 670 K depending on the used kinetic reaction model. This quick temperature increase during tank loading is due to absorption exothermic reactions and hydrogen compression process which produce heat. Then, it slows down gradually and becomes equal to the cooling temperature of 300 K.

The figure 6 shows stratified isothermal contours when x = 50 mm at 52 s using the kinetic reaction method of JMAK. In addition, significant temperature gradients were recorded between the tank surface and its center. These thermal gradients are axial and radial. The temperature reaches a maximum value at the center of the tank, and is lower in the area close to the wall. Finally, the results showed little differences between temperature contours when changing kinetic reaction models.

The figure 7 shows hydrogen capacity profiles with different kinetic reaction equations. Indeed, the hydrogen capacity increases gradually during the first 73 seconds. Then, it becomes constant after reaching its maximum value.

Since the JMAK method is the mostly used in comparative studies with experimental data, the obtained results show that the CV-2D is the most suitable method in such a case as compared to the other models.

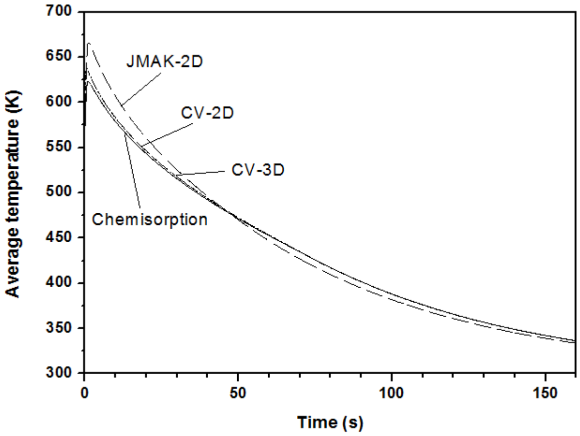


Figure 5: Absorption average temperature profiles with the different kinetic equations methods with $\Delta t = 0.01$ s and at supply pressure of 1 MPa.

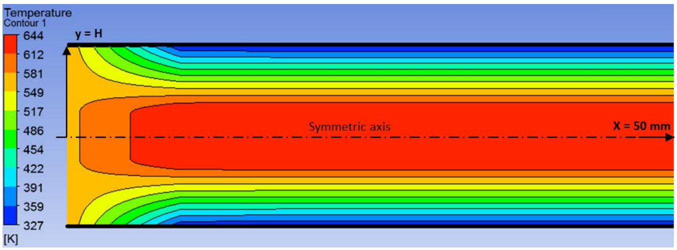


Figure 6: Average bed temperature contours at absorption time t = 52 seconds and x = 50 mm with JMAK method (horizontal line is the symmetric axis of geometry).

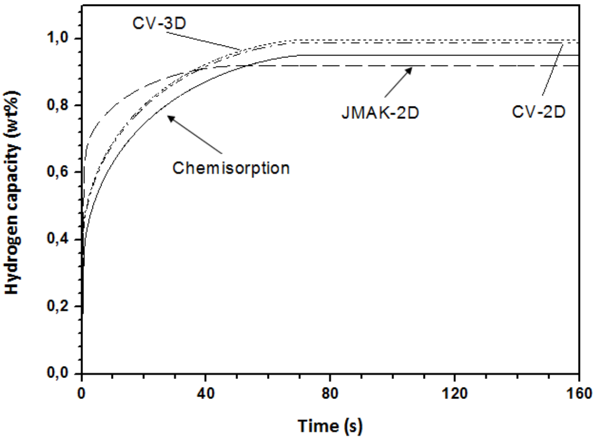


Figure 7: Hydrogen storage capacity profiles at supply pressure of 1 MPa with different methods.

## 5 Conclusion

In this numerical study, the thermal behaviour of a two-dimensional metal hydride tank has been explored by solving the relevant equations for heat transfer. Four different models have been introduced for the kinetic reactions in porous bed (metal hydride) in the framework of Fluent simulations. Fluent uses the finite volume method to discretize the equations generated from the mathematical model. The validation has been achieved by comparing the obtained results with experimental data.

Results have shown an important and quick generated heat at the beginning of the hydrogen absorption process into metal hydride. These temperature gradients between the center and the surface of the tank are axial and radial. Also, little differences between temperature contours were noticed when changing kinetic reaction models.

The use of different equations to model the kinetics of reaction has been found to produce almost similar results. However, the most suitable method for our two-dimensional study is a CV-2D technique because it generates the smallest error especially during the beginning of the reaction. Also, its computational time is the shortest one compared to the other methods (e.g., the JMAK)

Further work is in progress to extend the present study to the effective threedimensional configuration.

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