

Testing of Locally Available Jordanian Materials for Hydrogen Storage

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Abstract

Several locally available materials were tested for hydrogen storage. This study was conducted theoretically using suitable software. The materials tested were Sweileh sand, Zeolite, Nickel, Magnesium and Lanthanum. It was found that using the locally available Sweileh sand alone did not give promising results. Pure Magnesium showed the best results followed with Nickel then Lanthanum. On mixture basis, adding Magnesium to local Sweileh sand improved its storage ability more than adding other materials like Ni or La.

Keywords: metal hydride, hydrogen storage, fuel cell, solid hydrogen storage

1. Introduction

The increase in energy consumption particularly in the past several decades has raised fears of exhausting the globe's reserves of natural resources in the future. Due to industrialization and population growth as well as influx of refugees from neighboring conflict areas, today, Jordan largely depends upon natural resources, which are not replaceable. Approximately 90% of Jordan's energy consumption comes from fossil fuels.

The primary energy consumption consists of Natural gas, crude oil and oil products, imported electricity and renewable energy. The bulk of the consumption in 2011 being Crude oil and related products (Khammash, 2012).

Natural gas is utilized by the Kingdom to generate electricity, with some 80% of the electricity produced in Jordan depending on the imported gas from Egypt. This is shown below in Figure (1 and 2).

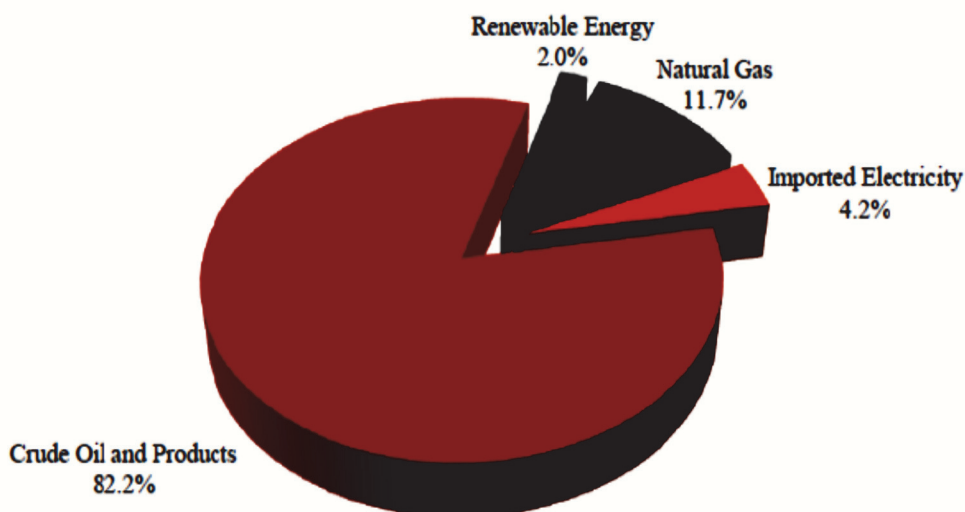


Figure 1. Composition of Primary Consumption in 2011

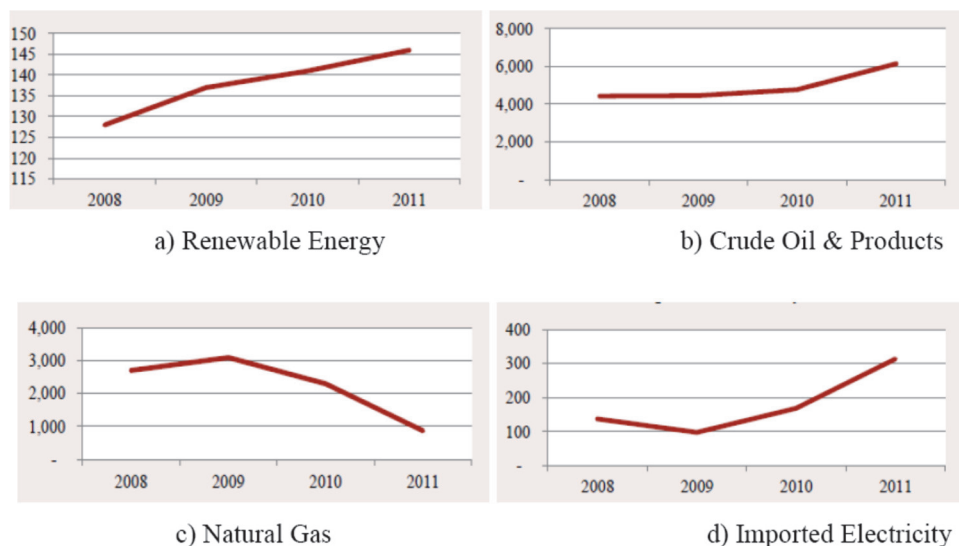


Figure 2. Primary Energy Consumption in Jordan

The disruption in the supply of natural gas to the Kingdom, which led to a decline in the amounts imported of around 65% in 2011 compared to 2010, coupled with the increasing burden of the high oil prices, have highlighted the urgency of persevering with the energy master plan to diversify the sources of energy going forward. In 2011, the total cost of imported crude oil, oil products and natural gas reached a whopping JOD3.84 billion, up by 51% compared to 2010.

The main objective of this paper is to investigate a potential improvement to hydrogen storage materials for fuel cells using locally available sources in Jordan. It also aims to improve the mathematical model used worldwide with the aim of adding to its accuracy. There are many available materials in Jordan that we can use in Hydrogen storage such as:

1.1 Silica Sand

Silica sand is defined as a high purity industrial mineral in which the sand grains are made entirely of quartz. Impurities are very minor. The term silica sand is applied to quartz sand that conforms to the specifications of which the main composition is $\text{SiO}_2 > 99\%$, with very little contaminant oxide contents (i.e., Al_2O_3 , TiO_2 , CaO , and Fe_2O_3) and heavy minerals of $< 0.1\%$.

The granules of silica absorbed hydrogen readily and withstood many hydrogen absorption cycles without producing fines. The porosity of the silica matrices was optimized so that the pores were large enough to allow hydrogen to easily move within the matrix and react with the metal hydride particles, but small enough to act as a filter to prevent passage of larger molecule including harmful impurities.

Silica sand are located at Ras En Naqb Area, Petra / Ein El Biada Area, Al Jayoshia Area and Qa'a Ed Disi Area which have the highest reserve (Madanat, Kailani & Mehyaar, 1998).

1.2 Zeolite

Zeolites from a large group of hydrous silicates that show close similarities in composition, association, and mode of occurrence. They are framework aluminosilicates with Na and Ca, and highly variable amounts of H_2O in the voids of the framework.

Porous materials have shown that their high surface areas are useful in the desorption of hydrogen. Zeolite absorbs a small amount at room temperature and ambient pressures, meaning it would be an incurred energy cost from maintaining low temperatures and elevated pressures in use. It could be used to enhance pressurized storage systems, and clearly low weight frameworks. The chemical tuning available in zeolites could allow for improved binding of hydrogen.

Zeolitic tuffs are located at Jabal Aritayn (30km NE of Azraq), Tlul Al-shahba (20km E of Al safawi), Tell-Rimah (35km NE of Al Mafrq) and many other small deposits in south and Central of Jordan (Jemni, Nasrallah & Lamloumi, 1999).

2. Mathematical Model

Before describing the mathematical model and its modifications, the following assumptions are used :

1. Storage is symmetric along the vertical (Z) axis.
2. Thermal equilibrium between solid and gas volumes,
3. Pressure variation in the tank is small, hence, neglected.
4. The effect of the hydrogen concentration on the equilibrium pressure variation is negligible (flat desorption and absorption plateaus on the P-C diagram).
6. The advection terms in the energy equation can be neglected.
7. Hydrogen behaves as an ideal gas.

The first assumption adequately approximates the physical scenario being modeled here since there is likely to be little variation in the convection coefficient or temperature values along the perimeter of the exterior tank walls.

The second through fifth assumptions were validated by two through five are validated by Jemni and Ben Nasrallah (Kikkinides, Georgiadis & Stubos, 2006). The sixth assumption is a consequence of the third assumption.

As can be concluded from the literature review, 2D models have been found to adequately represent hydrogen adsorption/desorption processes without extra computational complexity. Therefore, present work considers two-dimensional axisymmetric cylindrical geometry. A metal hydride reactor comprises both an expansion volume of length L_g and a bed filled with a LaNi₅ metal hydride alloy of length L .

The bed and expansion parts are surrounded by a jacket with the cooling fluid flowing in it. The hydrogen gas enters the storage tank from the cylindrical inlet of the specified radius R_f . In the study of Kikkinides et al. (2006) the heat exchange configuration consisting of additional concentric annular ring and tube demonstrated significant improvement for the hydrogen storage time optimization. Thus, for the current research the same heat exchange system within the bed has been used as shown in Fig. (3):

HE1- inner tube heat exchanger filled with cooling fluid and placed in the center of the reactor from $r=0$ to $r=r_0$;

HE2- inner annular ring heat exchanger for which thickness is specified as $\delta r=r_2-r_1$ (filled with cooling medium);

HE3- outer surface heat exchanger of radius r_3 that surrounds both the expansion volume and porous media.

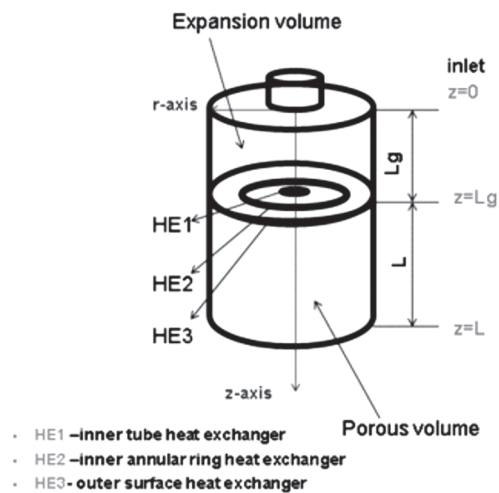


Figure 3. Metal hydride reactor with heat exchangers (in black) inside and outside of the bed

Basic Modeling Equations

There are many mathematical models in the literature on metal hydrides. All these models describe the same processes that take place during adsorption and desorption in a metal hydrogen reactor. However, significant differences occur in the models presented by different authors due to the scope of model consideration, the presence of additional assumptions, model dimensions, etc. Since 2D models are of particular interest for this research project, some basic modeling equations are discussed below.

2.1 Porous Volume

Mass balance

General mass balances for hydrogen (Eq. 1) and solid (Eq. 2) depending on the r and z axes

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

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

Energy balance

Energy balances for metal hydride beds (Eq. 3) can be expressed as a single equation if the assumption of local thermal equilibrium is valid and used for model development.

$$(\rho_g \cdot C_p)_e \cdot \frac{\partial T}{\partial t} + \rho_g \cdot C_{pg} \cdot u_r \frac{\partial T}{\partial r} + \rho_g \cdot C_{pg} \cdot u_z \frac{\partial T}{\partial z} = \frac{1}{r} \cdot \frac{\partial}{\partial r} \left(r \cdot \lambda_e \cdot \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(\lambda_e \cdot \frac{\partial T}{\partial z} \right) - m \cdot (\Delta H^\circ - T(C_{pg} - C_{ps})) \quad (3)$$

Where;

$$(\rho_g \cdot C_p)_e = (\varepsilon \cdot \rho_g \cdot c_{pg} + (1 - \varepsilon) \cdot \rho_s \cdot c_{ps})$$

$$\lambda_e = \varepsilon \lambda_g + (1 - \varepsilon) \lambda_s$$

In case if the temperatures of solid and gas phases are not equal, a single energy equation is not sufficient to determine the temperature field in the reactor so that energy balances are derived separately.

Momentum balance

The gas velocity is calculated using either Darcy's law (Eq. 4), i.e. the axial and radial pressure drops depend linearly on the superficial velocity, or more detailed z - and momentum balances. In most of studies reviewed, the Blake-Cozeny equation is used for the model development:

$$u = -\frac{k}{\mu} \text{grad}(P) \quad (4)$$

2.2 Expansion Volume

Mass balance

The differences between expansion and porous volume mass balances can be easily determined. In case of expansion compartment of the metal hydride reactor, there is no hydrogen adsorbed or desorbed, thus m is equal to 0, and there is no need to account for the volume porosity since it comprises the gas phase only. This is shown in (Eq.5)

$$\frac{\partial \rho_g}{\partial t} + \frac{1}{r} \cdot \frac{\partial}{\partial r} (r \cdot \rho_g \cdot u_r) + \frac{\partial}{\partial z} (\rho_g \cdot u_z) = 0 \quad (5)$$

Energy Balance:

Energy balance can also be written as follows :

$$\rho_g \cdot C_{pg} \cdot \frac{\partial T}{\partial t} + \frac{1}{r} \cdot \rho_g \cdot C_{pg} \cdot u_r \cdot \frac{\partial}{\partial r} (r \cdot T) + \rho_g \cdot C_{pg} \cdot u_z \cdot \frac{\partial T}{\partial z} = \frac{1}{r} \cdot \frac{\partial}{\partial r} \left(r \cdot \lambda_g \cdot \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(\lambda_g \cdot \frac{\partial T}{\partial z} \right) + \frac{\partial P}{\partial t} \quad (6)$$

2.3 Other Governing Equation

Reaction kinetics

Based on previous studies (Kikkinides, Georgiadis & Stubos, 2006; Kaplan & Veziroglu, 2003), the following reaction kinetics is used for the modeling of the LaNi₅-H₂ system:

-for hydriding case

$$(1 - \varepsilon) \cdot \frac{\partial \rho_s}{\partial t} = C_a \cdot \exp \left(-\frac{E_a}{R_g \cdot T_s} \right) \cdot \ln \left(\frac{P}{P_{eq}} \right) \cdot (\rho_{sat} - \rho_s) \quad (7)$$

- for dehydriding case

$$(1 - \epsilon) \cdot \frac{\partial \rho_s}{\partial t} = C_d \cdot \exp\left(-\frac{E_d}{R_g T_s}\right) \cdot \left(\frac{P - P_{eq}}{P_{eq}}\right) \cdot \rho_s \quad (8)$$

Where ρ_{sat} is the density of the saturated metal hydride bed, i.e. after the reaction is completed.

The equilibrium pressure was calculated using the following equation:

$$\ln(P_{eq}) = \frac{\Delta H}{R_g T} - \frac{\Delta S}{R_g} \quad (9)$$

2.4 Modification of Model

The modifications applied to the above model include :

1. Specific heat for Hydrogen gas was taken as function of temperature.
2. Viscosity variation as a function of hydride bed temperature.
3. Equivalent thermal conductivity as a function of diameter of hydride material.
4. Pressure of gas according to Darcy law is combined with momentum equations.

2.5 Initial Conditions

Initially the pressure, the temperature, and the metal hydride density in the tank are assumed to be constant, the tank is fully charged, and is in a state of equilibrium:

$$T(r, z, 0) = T_i, \quad P_g(r, z, 0) = P_i \quad \text{and} \quad P_s(r, z, 0) = P_i$$

2.6 Boundary Conditions

$$\text{Top surface boundary conditions:} \quad P_g = P_t \quad \text{and} \quad T = T_t \text{ or } K_t \frac{\partial T}{\partial z} = q_t''$$

$$\text{Centre axis boundary conditions:} \quad P_g = P_c \quad \text{and} \quad T = T_c \text{ or } K_c \frac{\partial T}{\partial r} = q_c''$$

$$\text{Side surface boundary conditions:} \quad P_g = P_s \quad \text{and} \quad T = T_s \text{ or } K_s \frac{\partial T}{\partial r} = q_s''$$

$$\text{Bottom surface boundary conditions:} \quad P_g = P_b \quad \text{and} \quad T = T_b \text{ or } K_b \frac{\partial T}{\partial z} = q_b''$$

The following table (1) shows the properties of the materials were used in the simulation models in all of its stages.

3. Results and Discussion

Figures (2) show the model output for general LaNi₅ material. The aim was to test the validity of the model. The model was found to predict the behavior of the tested hydride material as shown in [5].

This part discusses the initial screening test done to choose the best suitable material. In this part, several materials were selected and modeled for the hydrogen storage under the same conditions to try to find the best performing materials.

The main criterion for the selection used was the ability to store at moderate temperatures and pressures as well as less time. Other criteria which may be used for the selection can be the volume of canister needed to store certain amount of hydrogen.

In this project the first two were selected. The materials used in this study were selected after thorough search in the available literature as well as the available materials locally in Jordan. Modeling was done with the help of specialized software designed for fuel cell testing e.g. PDESol.

Table 1. Properties of Materials Use in Modeling

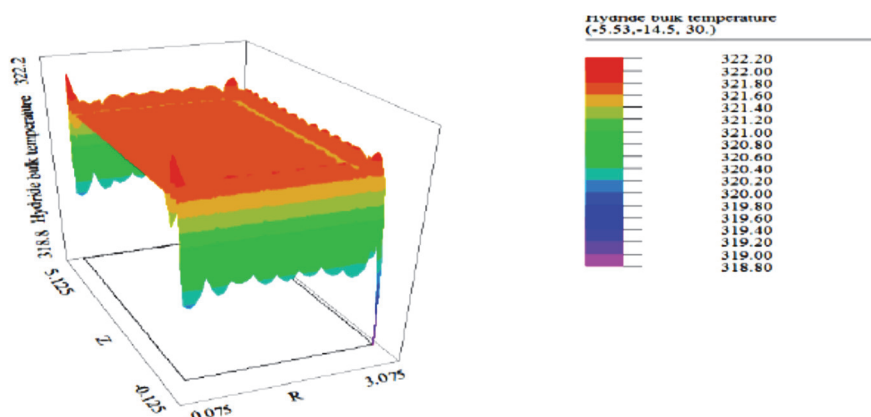
Materials	Thermal conductivity (W/mK)	Specific heat (J/kg.K)	Density (kg/m ³)	Young's modulus (GPa)	Poisson ratio
Lanthanum	13.4	190	6162	36.6	0.28
Magnesium	156	102	1738	45	0.29
Nickel	90.9	440	8908	200	0.31
Sand	0.2452	710	830	-	-

The results of the initial screening is presented below in Figures (3). The hotness of the materials refer to the absorption reaction between the material and hydrogen. As can be noticed, Sweileh sand and Magnesium showed the best performance (though at the cost of high temperature) and the best storage capacity compared with other materials like Nickel and Lanthanum.

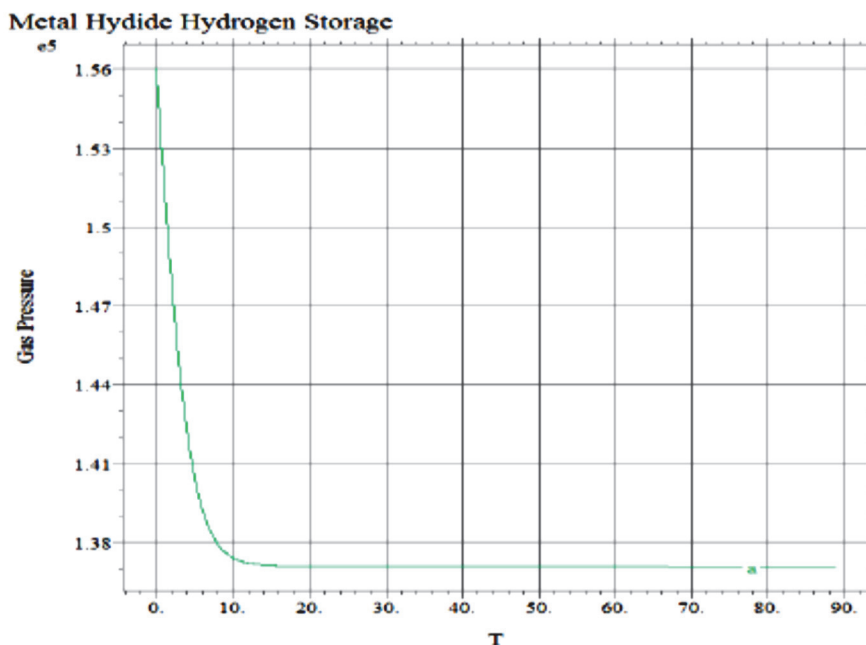
Though Lanthanum showed relatively cooler behavior, however the storage capacity was not as showed by other materials.

Therefore, the three best performing materials selected for the next screening test were Magnesium, Lanthanum and Sweileh sand. The next step taken in this project was the attempt to find the best combination between the two selected materials.

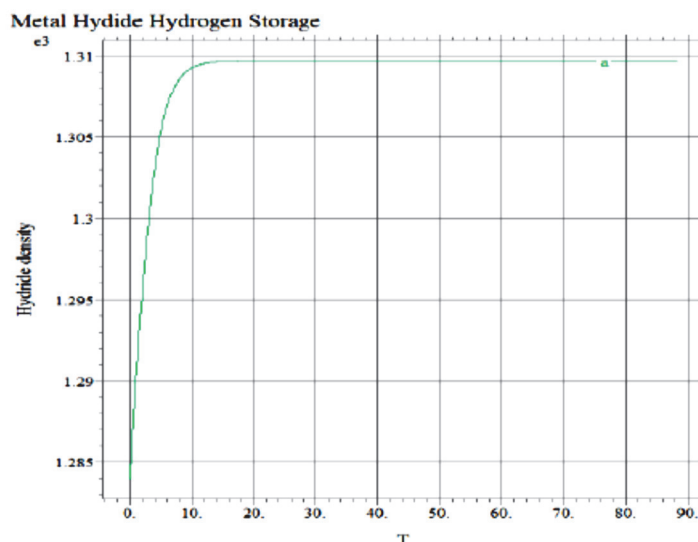
As an initial test, mixtures of 50-50% was selected and their respective properties were calculated by linearly interpolating the properties of each one.



(a) Temperature distribution in the canister.



(b) Hydrogen gas pressure variation with time



(c) Metal hydride density variation with time

Figure 4. Model output data

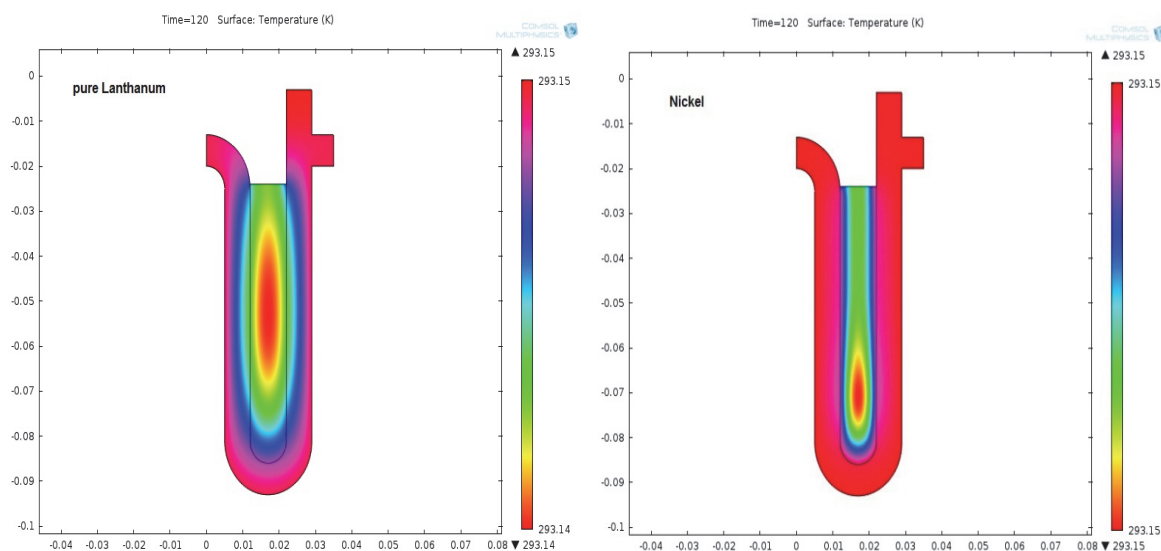
These data were fed to the model and the results were as shown in Figures (4). It was clearly shown that the addition of sand to Lanthanum and Magnesium was an added advantage because as shown, it showed best storage capacity at lower temperatures. The combination of Lanthanum and Magnesium did not show competitive results as shown by others.

The last step in this initial screening was to find out which is more effective in hydrogen storage, is it the Sand or other materials. For this purpose, 25-75% of the materials mixtures were selected and again their respective properties were calculated by linear interpolation.

As clearly shown in Figures 4 the addition of Magnesium was more effective to the adsorption reaction than that of Sweileh sand. This is in total agreement with the available literature.

According to Temperature distribution, the amount of absorption of hydrogen is better when we use the higher percentage of Magnesium.

The original model was modified with the use of variable specific heat and viscosity equation for hydrogen to accommodate for the temperature and pressure change during the process. Figures (5, a, b, c, d and e) show the temperature variation throughout the absorption process.



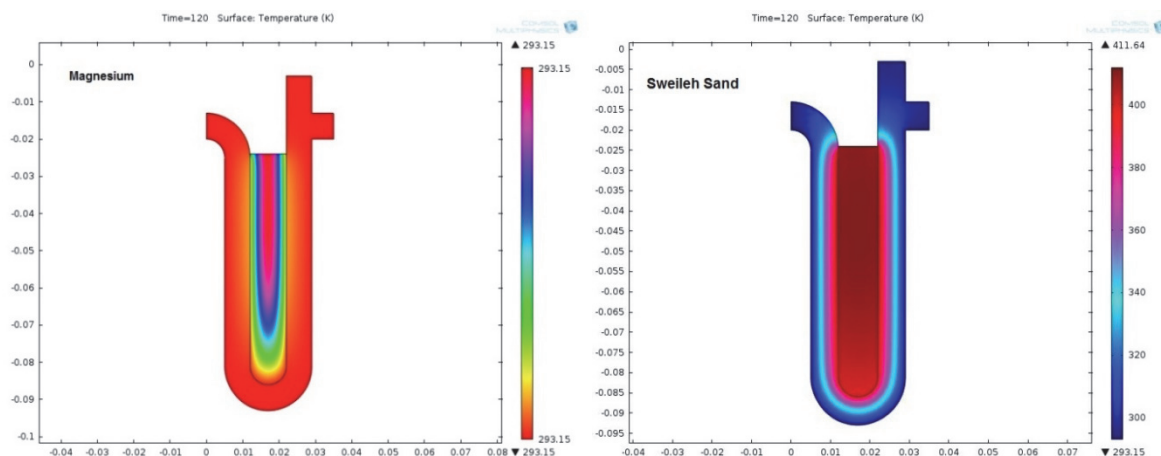
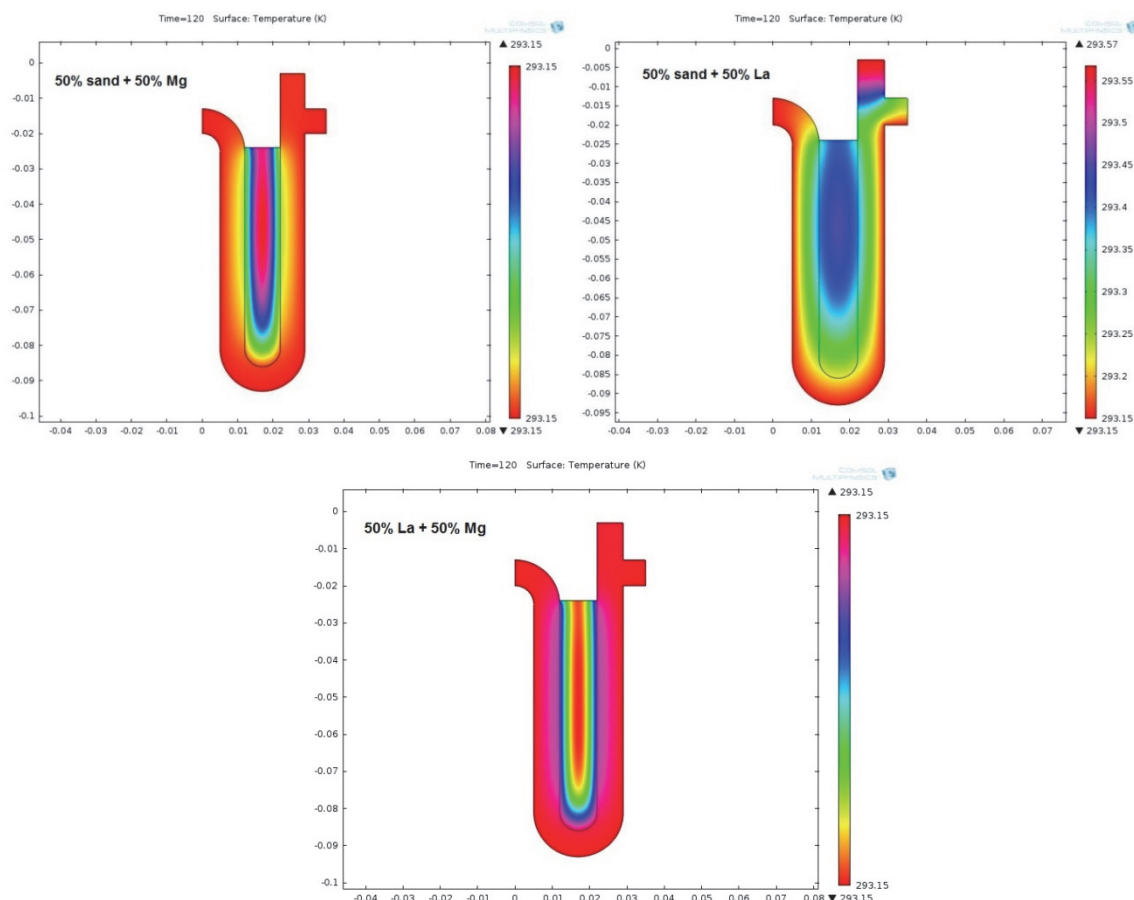


Figure 5. The amount of absorption for different pure materials

It is clearly noticed that Magnesium was the most uniform with maximum temperature rise during the adsorption process. This is clear indication that the amount of reaction that took place with Mg was higher than others. This means that the amount of hydrogen stored was higher than other materials. This is a clear advantage of the material as it will help in easily release the stored hydrogen during the desorption process. This is clearly shown in Figure (5-a).

Sand, on the other hand, shown in Figure (5-b), showed relatively lower temperature rise compared with Mg. This means that the amount of hydrogen stored was low compared with Mg. And hence, less hydrogen will be evolved during the desorption process. This is expected since the properties of sand are not as superior as that for Mg. This is shown in Table (1).



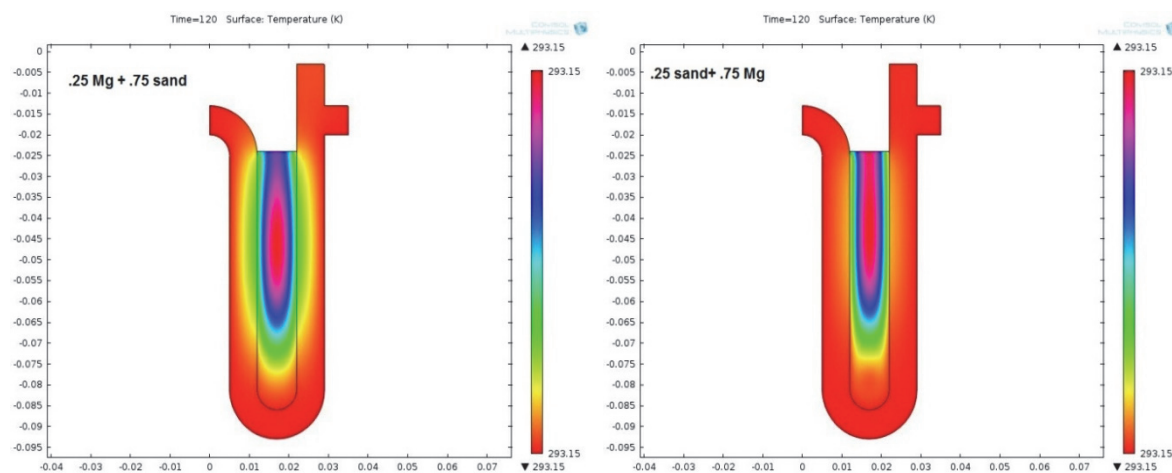
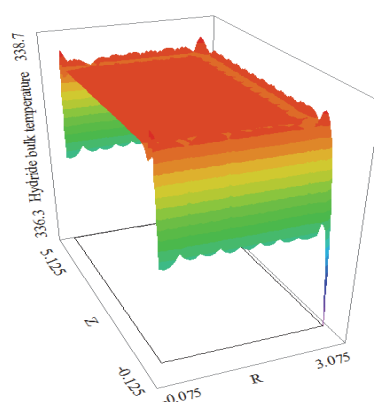


Figure 6. The amount of absorption for different percentage of sand and Mg mixture

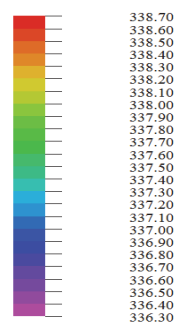
a) Magnesium (pure)

Metal Hydride Hydrogen Storage

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FlexPDE 5.0.21



Hydride bulk temperature
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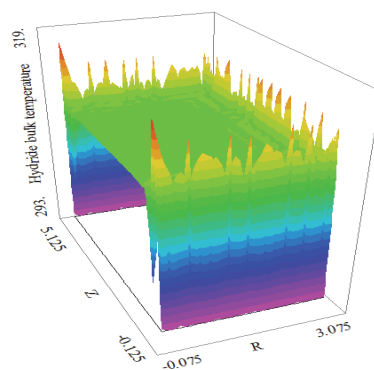


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Vol_Integral= 47843.92

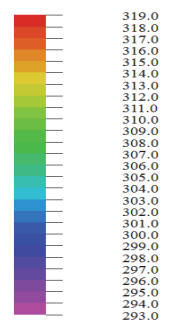
b) Sand (pure)

Metal Hydride Hydrogen Storage

12:46:08 10/26/13
FlexPDE 5.0.21

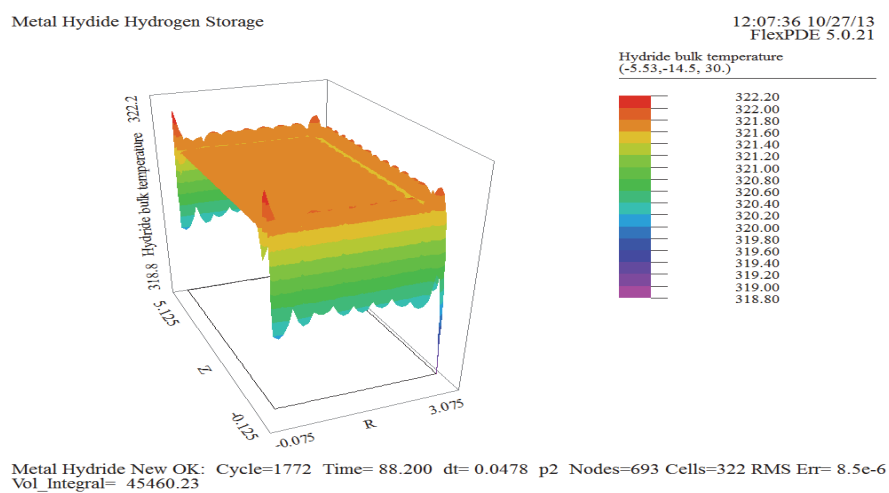


Hydride bulk temperature
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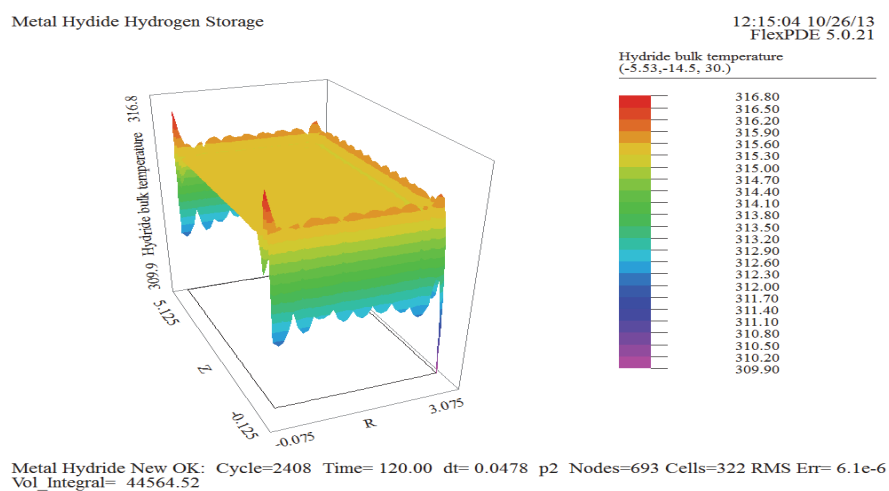


Metal Hydride New OK: Cycle=2413 Time= 120.00 dt= 0.0490 p2 Nodes=807 Cells=368 RMS Err= 1.7e-7
Vol_Integral= 43720.91

c) 50% sand, 50% Mg



d) 75% sand, 25% Mg



e) 25% sand, 75% Mg

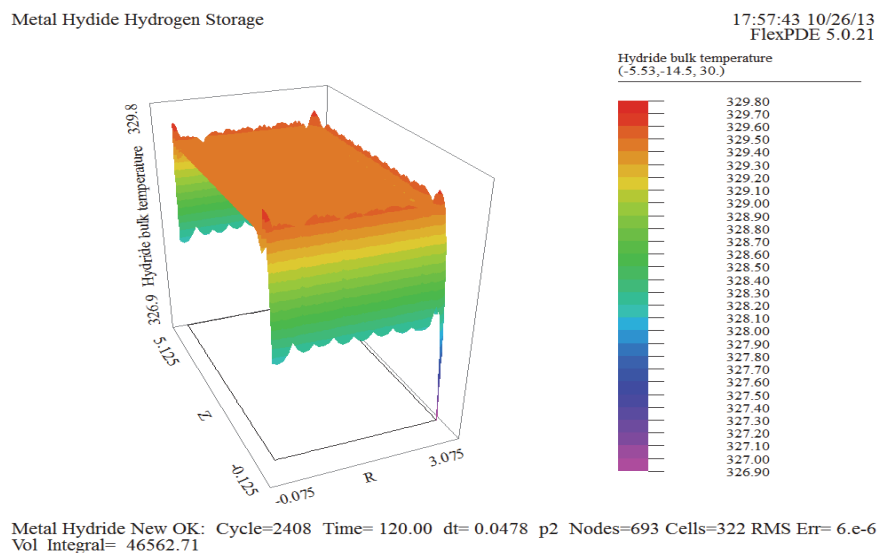


Figure 7. Temperature Variation throughout the Absorption Process

Figures 7 further show that the absorption properties improved with the addition of Mg in the mixture. This is expected since the addition of Mg improves the absorption kinetic reaction. Based on the samples studied, 75%MG + 25% Sand was the best.

4. Conclusion

After studying the different materials available in Jordan it is concluded that no single material shall be used for hydrogen storage; rather a mixture of several materials may be better for good hydride performance. It is also concluded that Mg is recommended to be used with other materials for better hydrogen storage capacity.

Acknowledgement

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