Performance Investigation of Multi-Stage Hydrogen-Based Sorption Heat Pump

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Metal hydrides are broadly investigated, for more than three decades, towards its application for cooling and heating applications. As a continuation of those works, in the present study, authors have investigated the performance of a multi-stage sorption heat pump for multiple cooling and heating outputs. The metal hydrides selected for the present study are $Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$, $MmNi_{4.7}Al_{0.3}$, $LaNi_{4.8}Al_{0.2}$ and $Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$, with the operating temperature range as 20°C for cooling output, 45°C for heating output and 140°C for heat supply. The system produces three cooling and four heating outputs with only one heat input. The performance of the system is investigated, via finite volume approach, in terms of hydrogen interaction within the coupled beds, bed temperature variations and heat interactions during hydrogen transfer processes. The minimum temperature observed during the cooling process is 0.5°C, whereas the maximum temperature observed during the heating process is 60°C, which shows that the obtained temperature is capable of space air-conditioning. On the other hand, the maximum cooling and heating outputs, at a particular instant of time, are estimated at 361 W and 402 W, respectively with a heat supply of 23 W.

Keywords: *hydrogen storage; heat pump; finite volume method.*

1. INTRODUCTION

Recently, a lot of research work has been carried out on metal hydrides, and they have been proved to be a good alternative for using in cooling and heating systems and hydrogen compressor. Moreover, metal hydrides have been successfully used for thermochemical energy storage applications. Compared to conventional vapour compression refrigeration systems, which need high-quality energy for their operation, systems based on sorption phenomena are a more environment-friendly and efficient option. This is because they can be operated using low-level energy in the form of waste heat from other systems or solar energy [1]. Its use of hydrogen as working fluid replaces the need for harmful refrigerants. To achieve a more extensive range of working temperature and with improved efficiency, multistage metal hydride based sorption system can be employed, which further opens up the opportunity to get multiple heat outputs. For the purpose, the selection of good working pairs is vital. A lot of theoretical and experimental research work has been carried out to determine excellent performing working pairs for use in single as well as multi-stage metal hydride sorption based thermodynamic systems.

Sandrock [2] comprehensively reviewed the hydrogen storage capabilities in addition to the reaction kinetics of materials such as alloys, complex hydrides, natural elements and carbon-based materials. The study was conducted for the temperature range of 0-100°C and pressure range of 1-10 bars. It was concluded that Vanadium is the only suitable natural element for the given range of operating conditions. It was also reported that Metal Hydrides having AB_5, AB_2 and AB combinations show excellent pressure-concentration isotherms (PCI) properties at room temperature while the compounds having a combination of AB_2 and AB show functional H_2 storage capacity with a minimal material cost. Here, element A refers to rare earth and alkaline metals, while element B is generally a transition metal. On the other hand, Dantzer [3] analysed the properties of metal hydrides (MHs) based on their suitability for hydrogen storage purposes for the temperature range of 500 K. It was concluded that, by controlling the slope and hysteresis, the reaction kinetics could be altered and the storage capacity can be improved, and by varying the composition, the materials can cater to the needs of the future for energy storage.

A review on the use of metal hydrides for storing hydrogen, electrochemical processing, gas separation, etc., was presented by Sandrock & Bowman [4]. It was concluded that to make the use of hydrogen storage materials viable; there is a need for determination of materials with better reaction kinetics and hydrogen storage capacity compared to materials being used currently.

Rusman & Dahari [5] reviewed the recent improvements in the amount of hydrogen stored in metal hydrides. It was observed that storage capacity and reaction kinetics of materials such as metal hydrides and complex hydrides, etc., can be augmented by the addition of catalysts. Mohtad & Orimo [6] reviewed the use of metal hydrides for applications involving energy storage. The key improvements in the storage materials

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were reported, which could make their use as energy storage materials more efficient.

Dantzer and Orgaz [7] experimentally investigated metal hydride heat pump (MHHP) performance by developing a model which works on isothermal and isobaric modes with $LaNi_{4.77}Al_{0.22}/LaNi_5$ pair and found the Carnot efficiency to be around 80-90%. In another study [8], the working pair was selected based on entropy, reaction enthalpy, and having the higher transfer of hydrogen between the materials. It was observed that with $ZrMn_{2.8}/LaNi_{4.75}Al_{0.25}$ as the working pair, an optimum COP of 2.16 at an output temperature of 50°C was obtained. With $Zr_{0.7}Ti_{0.3}Mn_2/LaNi_{4.56}Mn_{0.44}$, a COP of 2.00 at 100°C was obtained, and with $NiZr/LaNi_4Al$, a maximum COP of 2.26 at 150°C was obtained. Orgaz & Dantzer [9] carried out a comparative study of two systems, binary heat pump (BHP) and ternary heat pump (THP). They observed that at all temperatures, the COP of the BHP system was found to be lower than the THP system.

Due to the necessity of concurrent cooling and heating outputs, from air-conditioning systems, at different locations, there is a necessity of development of a thermodynamic device which can produce concurrent cooling and heating outputs with a larger capacity. Because of this, the present study aims to investigate the performance of a multi-stage sorption heat pump for air-conditioning applications. In our previous study [10], we have proposed the concept of multi-stage sorption heat pump and investigated its thermodynamic and heat-mass transfer studies using the set of $Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$, $MmNi_{4.7}Al_{0.3}$, $LaNi_{4.8}Al_{0.2}$ and $Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$ metal hydrides. In the present study, the proposed thermodynamic system is adopted to investigate its performance by employing the metal hydrides chosen from literature as best suited pair, based on selection criteria for a given temperature range.

2. SELECTION OF WORKING MATERIALS AND SYSTEM DESCRIPTION

The metal hydrides for the present work is chosen by employing the properties of different metal hydrides, available in the literature, as shown in Table 1, in a computer code to obtain the best-suited working pair. The computer code is created to determine the best-suited metal hydride pair based on cooling and heating outputs while maintaining the optimum pressure difference between coupled beds to enable the maximum hydrogen interaction among them. The above technique is applied for the working temperature range of 20°C, 45°C and 140°C and the best-suited metal hydrides obtained are $Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$ (R1), $MmNi_{4.7}Al_{0.3}$ (R2), $LaNi_{4.8}Al_{0.2}$ (R3) and $Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$ (R4).

The detailed working principle of a multi-stage sorption heat pump is available in the authors' previous article [9]. The beauty of the present system is that it can produce three cooling and four heating outputs with one heat input. The heating and cooling outputs are obtained by the heat interactions involved in hydrogen absorption and desorption by metal hydrides which are exothermic and endothermic reactions, respectively.

A schematic diagram of a multi-stage sorption heat pump integrated with solar heat collection and air-conditioning application is shown in Fig. 1. The heat input required in the system can be fulfilled by solar thermal energy using concentrated solar collector, whereas the concurrent cooling and heating outputs can be supplied to the building for air-conditioning applications as per demand. The system serves as environmentally friendly because it runs without any harmful refrigerant as well as without any moving parts like compressor as required in conventional vapour compression refrigeration system.

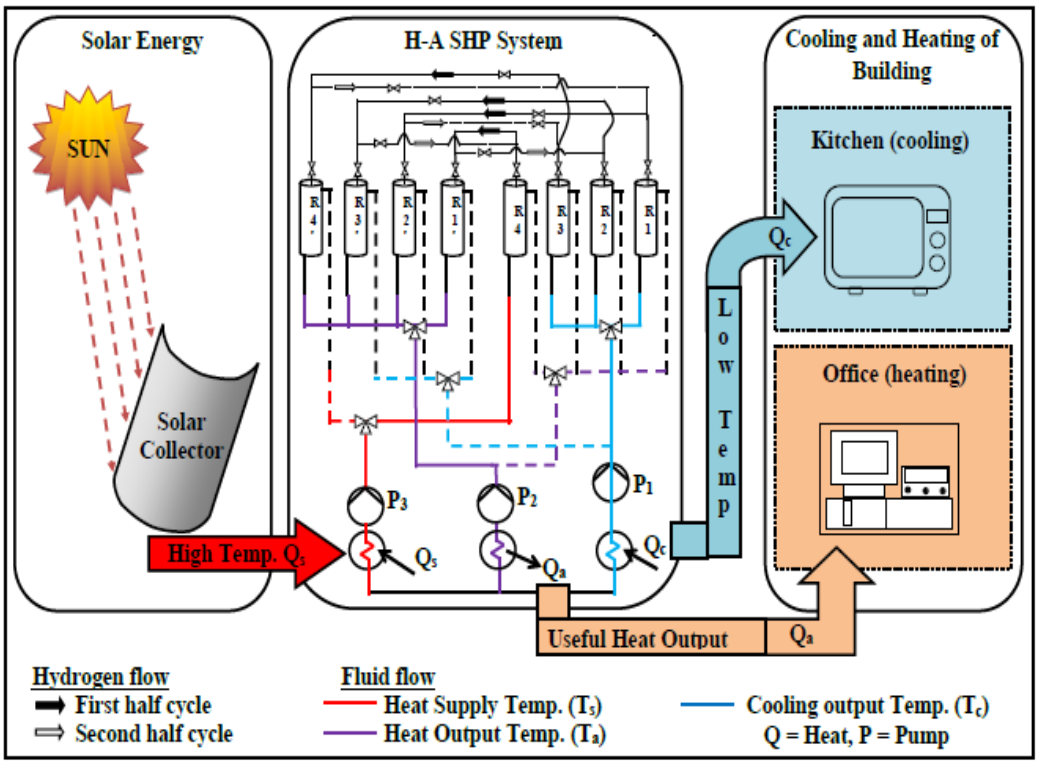

Figure 1. Schematic of multi-stage sorption heat pump for building air-conditioning [10]

Table 1. Properties of different metal

S. No.	Materials	Enthalpy (ΔH) (kJ/molH_2)	Entropy (ΔS) (J/K molH_2)	Maximum Storage Capacity (wt%)/Temp (°C)	Reference
1	$MmNi_{4.8}Al_{0.2}$	31.16	101.2	1.28/23	[11]
2	$LaNi_{4.7}Sn_{0.3}$	36.51	112.6	1.04/24.9	[12]
3	$MmNi_{4.7}Sn_{0.3}$	31.83	106.8	0.97	[12]
4	$LmNi_{4.9}Sn_{0.1}$	28.97	104.3	1.29/23	[11]
5	$MmNi_{4.7}Al_{0.3}$	27.50	107.6	1.21/23	[11]
6	$LaNi_{4.8}Sn_{0.2}$	31.3	101	1.28/22	[13]
7	$LaNi_5$	30.7	110	1.29/21	[13]
8	$MmNi_{4.9}Fe_{0.1}$	24.8	84.7	1.2	[14]
9	$MmNi_5$	20.3	101.4	1.44/20	[15]
10	$MmNi_{4.5}Al_{0.5}$	24.41	97.04	1.36/20	[15]
11	$MmNi_4Al$	26.17	79.9	1.30/20	[15]
12	$MmNi_{3.7}Co_{0.7}Mn_{0.3}Al_{0.3}$	33.11	96.94	1.16/20	[15]
13	$MmNi_{3.5}Co_{0.4}Mn_{0.4}Al_{0.4}Fe_{0.3}$	34.27	97.82	1.05/20	[15]
14	$La_{0.8}Ce_{0.2}Ni_5$	26.6	107.3	1.4/20	[16]
15	$La_{0.9}Ce_{0.1}Ni5$	32.9	121	1.3/40	[17]
16	$LaNi_{4.6}Al_{0.4}$	34.04	108	1.41/20	[18]
17	$LaNi_{4.7}Al_{0.3}$	32.7	105	1.22	[19]
18	$MmNi_{4.2}Al_{0.8}$	25.09	120	1.3/25	[20]
19	$LaNi_{4.85}Al_{0.15}$	31.6	106	1.25	[21] [22]
20	$MmNi_{4.85}Al_{0.15}$	21.05	93.9	1.4/20	[22]
21	$LaNi_{4.85}Sn_{0.15}$	29.8	105	1.3/30	[22]
22	$MmNi_{4.6}Al_{0.4}$	28	107.2	0.95/20	[23] [24]
23	$MmNi_{4.6}Fe_{0.4}$	27.5	105	1.15/20	[23] [25]
24	$LaNi_{4.5}Sn_{0.5}$	36	97	0.95/26.8	[26]
25	$Mm_{0.5}La_{0.5}Ni_{4.7}Sn_{0.3}$	33.8	111.2	-	[27]
26	$LaNi_{4.8}Al_{0.2}$	30.4	101.6	-	[27]
27	$MmNi_{4.7}Fe_{0.3}$	25.0	87.4	-	[27]
28	$TiFe_{0.9}Mn_{0.1}$	29.7	107.7	-	[27]
29	$La_{0.85}Ce_{0.1}5Ni_5$	24.3	91.28	-	[27]
30	$ZrFe_{1.8}Ni_{0.2}$	17.2	119.7	-	[27]
31	$Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$	27.4	112	1.5	[28]
32	$Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$	29.6	92.0	-	[29]
33	$Ti_{1.05}Fe_{0.9}Nb_{0.1}$	28.5	98.9	-	[30]
34	$Ti_{1.05}Fe_{0.8}Ni_{0.15}Cr_{0.05}$	42.5	120.6		[30]
35	$LaNi_{2.5}Co_{2.5}$	24.4	76.6	-	[30]
36	$LaNi_{2.5}Co_{2.4}Si_{0.1}$	27.6	81.9	-	[30]

3. METHODOLOGY

To investigate the performance of the sorption system, a finite volume approach is adopted. Since the present system involves hydrogen as well as heat transfer phenomenon, the fundamental governing equations, i.e. continuity, momentum and energy equations are solved. The partial differential equations are discretised to the algebraic equation by the fully implicit method. The computational fluid dynamics (CFD) analyses result in the variation in metal hydride bed temperatures, hydrogen transmission and heat interactions.

The modified Van't Hoff equation is used to determine the pressure variation within the bed during hydrogen transmission.

$$\frac{\Delta H}{R_u T} - \frac{\Delta S}{R_u} + \left(\phi \pm \phi_0\right) \tan\left[\pi\left(\frac{x}{x_f} - \frac{1}{2}\right)\right] \tag{1}$$

The hydrogen transmission to and from metal hydride beds are estimated using the following equations:

$$\dot{m}_d = C_d \exp\left(\frac{-E_d}{R_u T_d}\right)\left(\frac{P_{e,\,\mathrm{d}} - P_{g,t+\delta t}}{P_{e,\,\mathrm{d}}}\right)\rho_{m,\,\mathrm{d}} \tag{2}$$

$$\dot{m}_a = C_a \exp\left(\frac{-E_a}{R_u T_a}\right)\ln\left(\frac{P_{g,t+\delta t}}{P_{eq,a}}\right)\left(\rho_{SS} - \rho_{m,a}\right) \tag{3}$$

The deviations in metal hydride beds temperature are estimated by using the following equation:

$$\left(\rho C_P\right)_e \frac{\partial T}{\partial T} + \left(\rho C_P\right)_g \vec{u}.\nabla T = \lambda_e \nabla^2 T + \dot{m}_a\left[\frac{\Delta H}{M_g} - T\left(C_{p,g} - C_{p,m}\right)\right] \tag{4}$$

4. RESULTS AND DISCUSSION

The prediction of the system performance through CFD analysis in terms of metal hydride bed temperature, hydrogen interaction and heat interaction in cooling, regeneration and heating processes are discussed in this section. At first, all the metal hydrides are maintained at predetermined temperatures, as soon as the respective valves open, the deviation in beds temperatures can be expected as a result of exothermic absorption and endothermic desorption processes. The cooling effect can be utilised from the desorption enthalpies of beds R1, R2 and R3 at 20°C. As a result of desorption enthalpies, the sudden fall in bed temperatures can be seen in Fig. 2.

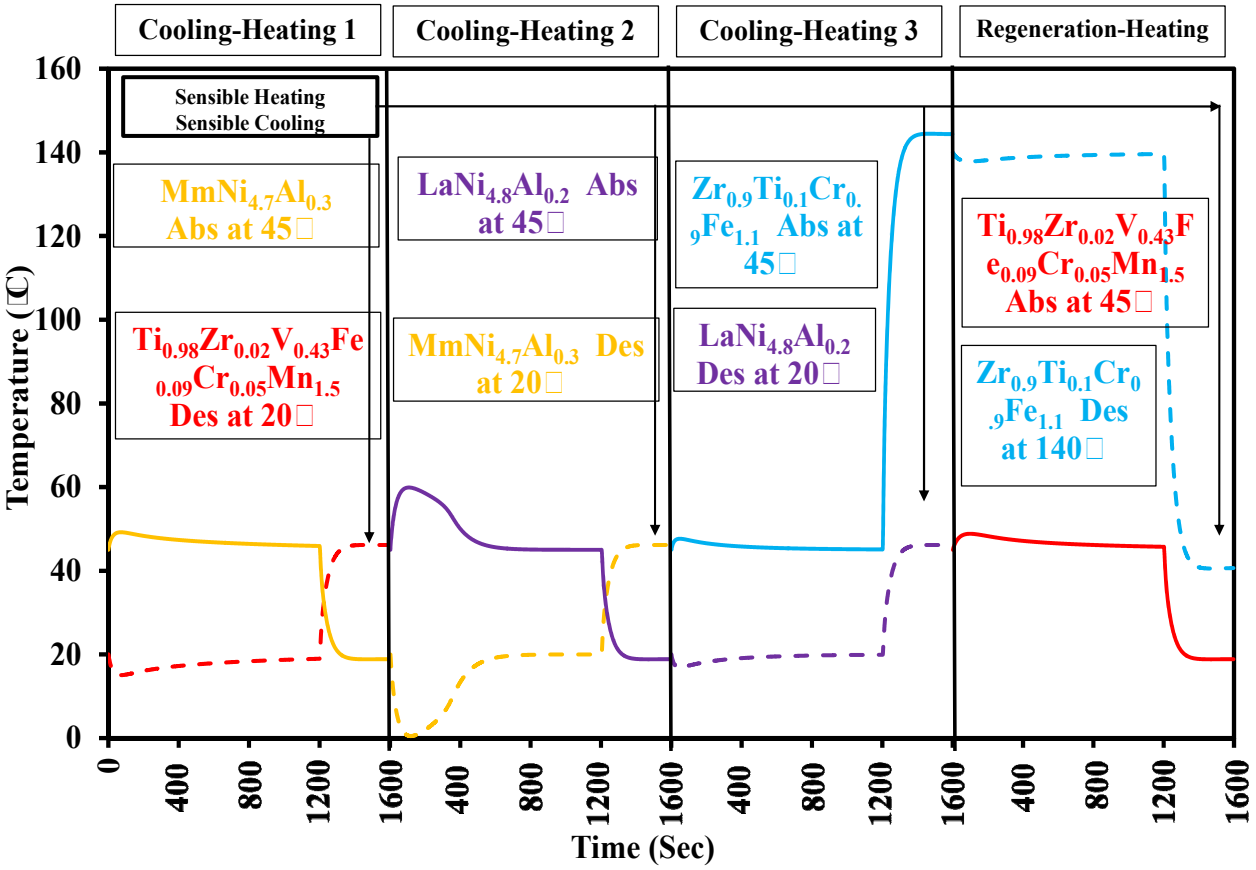

Figure 2. Bed temperature

Table 2. Metal hydride bed temperatures

Process	Coupled beds	Minimum bed temperature during cooling process	Maximum bed temperature during heating process
Cooling - Heating	$Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$ - $MmNi_{4.7}Al_{0.3}$	From 20°C to 15°C in 56 seconds	From 45°C to 49.2°C in 70 seconds
Cooling - Heating	$MmNi_{4.7}Al_{0.3}$ - $LaNi_{4.8}Al_{0.2}$	From 20°C to 0.5°C in 106 seconds	From 45°C to 60°C in 119 seconds
Cooling - Heating	$LaNi_{4.8}Al_{0.2}$ - $Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$	From 20°C to 15°C in 50 seconds	From 45°C to 47.6°C in 46 seconds
Regeneration - Heating	$Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$ - $Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$	From 140°C to 137°C in 70 seconds	From 45°C to 48.9°C in 80 seconds

The minimum and maximum temperatures of beds because of sudden fall and sudden upswing as a result of desorption (cooling process) and absorption (heating process) of hydrogen among coupled beds are shown in Table 2. Apart from the bed temperature deviations in hydrogen transfer processes, the bed temperature deviations in sensible heating and sensible cooling processes are also presented in Fig. 2.

On the other hand, the amount of hydrogen exchanged between paired beds for all the processes are shown in Fig. 3. During the selection of working pairs, it is assumed that there should be an optimum pressure difference between paired beds to provide maximum hydrogen exchange among them. In this way, the cycle time can be reduced as well as by increasing the hydrogen moles exchanged, the cooling and heating outputs can be increased. Since it is a four-stage system, it is challenging to obtain the high-pressure difference between the beds working for regeneration for a given temperature range; as a result, less hydrogen exchange occurs among them as shown in Fig. 3. This may reduce the overall useful output as well as COP. It is also observed that all the metal hydrides possess different reaction kinetics; therefore, to ensure the occurrence of complete processes, the simulation is conducted for 1200 seconds.

The cooling outputs are the result of desorption enthalpy, whereas heating outputs are the result of absorption enthalpies. Keeping this in mind, it will easy to understand that during desorption, a certain amount of heat will be absorbed from the heat transfer fluid whereas, during absorption, a certain amount of heat will be released to the heat transfer fluid. These heat interactions are shown in Fig. 4. The values of the maximum amount of heat absorbed from heat transfer fluid are 67 W, 188 W and 106 W, which can be considered as cooling outputs. Similarly, the values of the maximum amount of heat released to heat transfer fluid are 67 W, 190 W, 104 W and 41 W, which can be considered as heating outputs. During regeneration, it is 23 W which can be considered as heat supplied.

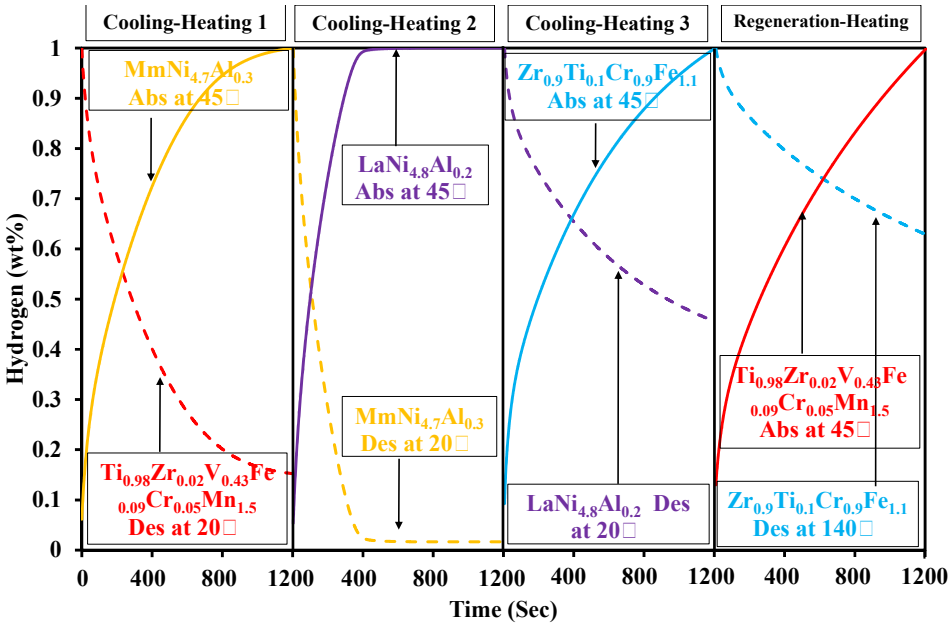

Figure 3. Hydrogen transmission

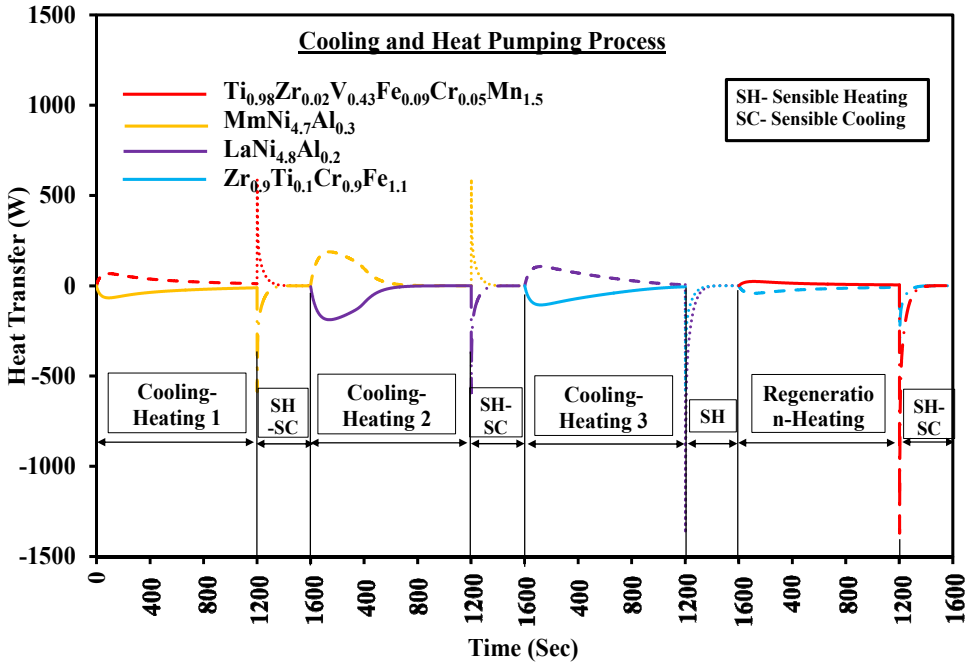

Figure 4. Heat interactions

5. CONCLUSIONS

The computational fluid dynamics analyses of a multi-stage sorption heat pump can be concluded with the following points:

1. To investigate the performance of sorption heat pump, $Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$, $MmNi_{4.7}Al_{0.3}$, $LaNi_{4.8}Al_{0.2}$ and $Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$ metal hydrides are chosen via computer code generated based on best performance parameters, i.e. optimum pressure difference and maximum amount of hydrogen exchange between coupled beds as well as maximum COP.
2. To investigate the performance of the system through the finite volume method, required governing equations are solved and discretised using a fully implicit method.
3. The numerical study results in 361 W of cooling and 402 W of heating with 23 W of heat supplied at a particular instant of time.
4. The minimum temperature of 0.5°C and a maximum temperature of 60°C is observed in cooling and heating processes.

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NOMENCLATURE

ΔH	Absorption/Desorption enthalpy, kJ mol^{-1}
ΔS	Absorption/Desorption entropy, kJ mol^{-1} K^{-1}
ϕ, ϕ_0	PCI slope factors
ρ	Density, kg m^{-3}
β	PCI Hysteresis factor
λ	Thermal conductivity, W m^{-1} K^{-1}
C_a	Absorption rate constant, s^{-1}
C_d	Desorption rate constant, s^{-1}
E	Absorption/Desorption activation energy, kJmol^{-1} of H_2
$\dot{m}$	Mass flow, kg m^{-3} s,
M	Molecular weight, kg $kmol^{-1}$
n	Moles of gas, mol
P_{eq}	Equilibrium pressure, bar
R_u	Universal gas constant, kJ mol^{-1} K^{-1}
T	Absolute temperature, °C
u	Velocity, m s^{-1}
wt%	Hydrogen concentration, %
x	Hydrogen concentration, (H/M ratio)

Subscripts

a	absorption
c	cold
d	desorption
e	equilibrium
g	gas
m	metal
ss	saturated

ИСТРАЖИВАЊЕ ПЕРФОРМАНСИ ВИШЕСТЕПЕНЕ АДСОРПЦИОНЕ ТОПЛОТНЕ ПУМПЕ НА БАЗИ ВОДОНИКА

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Истраживање примене металних хидрида за хлађење и грејање траје већ дуже од три деценије. У наставку даљих истраживања аутори се баве перформансама вишестепене адсорпционе топлотне пумпе, њених излазних перформанси хлађења и грејања.
Истраживања су обухватила следеће металне хидриде: $Ti_{0.98}Z_{r0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5}$, $MnNi_{4.7}Al_{0.3}$, $LaNi_{4.8}Al_{0.2}$ и $Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$ при чему је радна температура била 20^0C за излазну перформансу хлађења, 45^0C за перформансу грејања и 140^0C за довод топлоте. Систем производи три излазна хлађења и четири излазна грејања са само једним улазом топлоте. Коришћена је метода коначних запремина у истраживању интеракције водоника са одговарајућим слојем, варијацијама температуре у слојевима и током процеса преноса водоника. Најнижа температура у процесу хлађења износила је $0,5^0$C а највиша 60^0C, што показује да се са добијеном температуром може вршити климатизација простора. Максимална излазна перформанса хлађења и грејања износила је у одређеном тренутку 361W односно 402W а довод топлоте 23W.