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Performance analysis of a K₂CO₃-based thermochemical energy storage 1 system using a honeycomb structured heat exchanger 2 Karunesh Kant^{a*}, A. Shukla^b, David M. J. Smeulders^a, C.C.M. Rindt^a 3 ^aDepartment of Mechanical Engineering, Eindhoven University of Technology, 5600 MB-4 Eindhoven, Netherlands 5 ^bNon-Conventional Energy Laboratory, Rajiv Gandhi Institute of Petroleum Technology Jais, 6 Amethi, UP 229304, India 7 *k1091kant@gmail.com, 8 9

10 Graphical Abstract



11

12 ABSTRACT

The application of thermal energy storage using thermochemical heat storage materials is a promising approach to enhance solar energy utilization in the built environment. Potassium carbonate (K_2CO_3) is one of the potential candidate materials to efficiently store thermal energy due to its high heat storage capacity and cost-effectiveness. In the present study, a 3dimensional numerical model is developed for the exothermic hydration reaction of K_2CO_3 . The heat produced from the reaction is transferred indirectly from the TCM bed through the

19 walls of the honeycomb heat exchanger to a Heat Transfer Fluid (HTF). A parametric study is conducted for varying geometrical parameters of the honeycomb heat exchanger. The 20 21 obtained results indicate that the reaction rate and heat transport in the TCM bed strongly 22 depends on the geometrical parameters of the heat exchanger. Reducing the cell size of the 23 honeycomb heat exchanger up to a certain level provides better thermal transport as well as improved reaction rate of the TCM bed. The results of this study provide detailed insight into 24 the heat release processes occurring in a fixed bed of K_2CO_3 . The study is useful for 25 designing and optimizing thermo-chemical energy storage modules for the built environment. 26

27 Keywords: Thermochemical; Hydration; Thermal Energy, Reaction; Energy Storage.

28

29 Nomenclature

30	С	concentration [mol]
31	C _p	heat capacity [J/kgK]
32	D_g	water vapor diffusion coefficient [m ² /s]
33	d_p	particle diameter [m]
34	k	thermal conductivity [W/mK]
35	L _C	honeycomb cell length [m]
36	M_{v}	molar mass of water vapor [kg/mol]
37	p	pressure [Pa]
38	p_{eq}	equilibrium pressure [Pa]
39	R	ideal gas constant []/mol K]
40	$t_{gap,HTF}$	distance between two HTF tubes [m]
41	Т	temperature [°C]

42	и	Darcy velocity [m/s]
43	\mathcal{E}_{eff}	effective bed porosity
44	δ_{fin}	honeycomb fin thickness [m]
45	δ_b	bed height [m]
46	χ	stoichiometric coefficient
47	ρ	density [kg/m ³]
48		
49		

50 **1. INTRODUCTION**

51 Buildings are responsible for approximately 40% of the total energy consumption and for 36% of the total CO₂ emissions in the EU, ranking them at the top in terms of energy 52 requirements. [1]. As stated by the European Commission [2], about 75% of the heating and 53 cooling demand is still generated using fossil fuels while only 19% is generated from 54 renewable energy sources. To achieve the EU's climate and energy goals, the heating and 55 cooling sector must sharply reduce its energy consumption and also decrease the usage of 56 fossil fuels. Fossil fuels are not only depleting but are also responsible for global climate 57 change because of their induced rise in greenhouse gas emissions. Therefore, there is an 58 59 urgent need to focus on renewable energy sources for the heating purposes of buildings. The 60 application of renewable energy sources in the built environment is highly affected by the mismatch between the demand for energy and the supply of energy by renewable resources 61 62 like solar energy and wind energy. The seasonal mismatch, particularly in the case of energy demand for heating applications, can be resolved up to a large extent by utilizing seasonal 63 64 heat storage. The main idea is to store thermal energy in summer (high supply, low demand) and utilize it in winter (high demand, low supply). This can be achieved by developing 65 66 technologies that can efficiently store thermal energy for a longer period with minimal losses. The basic mechanism for developing such technology lies in the property of certain materials 67 68 that release heat when they ad/absorb water. This mechanism can be utilized to store heat from the sun by using solar heat to dry the material after water is absorbed. The energy stored 69 70 can be released later by simply adding water vapor to the material.

The thermochemical energy storage (TCES) materials as introduced above are promising 71 72 materials to store thermal energy utilizing a reversible chemical reaction [3-9]. In this 73 reaction, a thermochemical energy storage material (C) absorbs external heat (e.g. solar 74 energy, industrial waste heat) through an endothermic reaction, decomposing into A and B. Products (A and B) are separated by physical means and stored in separate containers. When 75 materials A and B are combined again, an exothermic reverse reaction, generation of C, and 76 77 release of stored thermal energy occur [10–14]. Although much work has been done in the 78 direction of material characterization, identification, and improvement, as well as process 79 integration and application, little effort has been put into closed thermochemical reactor 80 modelling and process design [15–17]. Funayama et al. [7] suggested the thermal decomposition of calcium hydroxide (Ca(OH)₂) into calcium oxide (CaO) and water vapor as 81

82 a reversible gas-solid reaction suitable for TCES. The study focused on the development of composite honeycomb support composed of silicon carbide and silicon to enhance the heat 83 transfer in a reaction bed. The results suggest that the heat transfer through the reaction bed 84 was enhanced by the Si-SiC honeycomb support. Zhou et al. [18] developed a numerical 85 model for TCES involving the energy balance and reaction kinetics describing the redox 86 reaction of cobalt oxides $(Co_3O_4/CoO \text{ pair})$, to simulate the phenomena of thermochemical 87 storage. Metallic redox pair oxides such as BaO_2/BaO , Mn_2O_3/Mn_3O_4 , CuO/Cu_2O and 88 Fe_2O_3/Fe_3O_4 have been studied for CSP plants [19,20]. Ranjha and Oztekin [21] performed 89 a numerical analysis of a three-dimensional bed with $Ca(OH)_2/CaO$ as the reaction pair. The 90 results of the study provide detailed insight into the heat release processes occurring in a 91 fixed bed of $Ca(OH)_2/CaO$ reaction pair. The study helps designing and optimizing high 92 temperature thermo-chemical energy storage modules for power generation applications. One 93 of the most promising chemical reaction systems for energy storage is the reaction utilising 94 potassium carbonate and water vapor [22]: 95

96

$$K_2CO_3(s) + 1.5H_2O(g) \rightleftharpoons K_2CO_3 \cdot 1.5H_2O(s) + 1.5\Delta H_r$$

97 Gaeini et al. [22] summed up the advantages of a $K_2CO_3 - K_2CO_3 \cdot 1.5H_2O$ system with a 98 storage capacity up to 96.015 kJ/mol (reaction enthalpy of ΔH_r ,= 64.01kJ/mol of water) 99 corresponding to a maximum energy density of 1.30 GJ/m³ [23,24]. It features high material 100 energy density and the reaction shows good reversibility. The drawbacks are that 101 thermochemical energy storage materials, in general, have low thermal conductivity. The 102 dehydration and hydration kinetics of the reactions involved are relatively well-identified.

103 This literature assessment indicates that numerical analysis, as well as experimental investigations of the TCES reactive materials and reactor design, has attracted considerable 104 interest during the past few decades. Although sensible and latent heat storage systems have 105 made their way into commercial applications, TCES (currently at the laboratory stage, mainly 106 107 due to technical challenges) could be applied in many applications [20,25,26]. Therefore, numerical simulation tools to model the thermochemical reactions, understand the reaction 108 kinetics, and optimize the system performance, are very essential. In the recent past, bionics 109 based tools have been realized to be one of the advanced tools, especially in the field of fluid 110 flow and heat transfer applications including chemical reactors [27], biomedical equipment 111 [28,29], and electronic cooling [30-34]. The fin structures made by natural assortment 112

encourage the improvement of the TCES device. By realizing natural structures, the fins with 113 bionic structures, for instance, tree-shaped fins [34,35], Koch fractal fins [36], and 114 snowflake-shaped fins [37,38], have been proposed by researchers for their enhanced heat 115 transport, subsequently increasing the thermal transport effectiveness of TCES devices. With 116 the existence of honeycomb meshed structures in nature, the idea surfaced to solve the 117 problem of thermal transport in a TCES device with the use of such a structure as a reactor 118 119 bed. Therefore, the present work focuses on the performance analysis of TCES based on potassium carbonate (K_2CO_3) filled in a honeycomb heat exchanger structure. 120

121 The performance analysis has been achieved by studying heat and mass transfer through the reactive bed of $K_2CO_3 \cdot 1.5H_2O$ designed for a thermochemical heat storage system. The 122 numerical model developed for the purpose has been solved using COMSOL Multiphysics 123 124 software [39]. The study is performed to see the impact of the honeycomb heat exchanger on the recovery of the thermo-chemically-stored energy as well as the reaction rate in the TCM 125 bed. Further, a parametric study has been conducted to investigate the effect of various 126 honeycomb heat exchanger design parameters (i.e. honeycomb cell size $[L_c]$, honeycomb fin 127 thickness $[\delta_{fin}]$, bed height $[\delta_b]$ and distance (denoted with subscript gap) in between two 128 HTF tube $[t_{gap,HTF}]$) on the temperature variation, the reaction advancement and the 129 recovery of the thermo-chemically-stored energy. These parameters are highly related to the 130 heat exchanger design of the honeycomb structure. It is explicitly noted here that the material 131 properties of potassium carbonate are considered to be constant during the reaction and that 132 133 resulting effects like swelling/shrinking are not taken into account.

The work performed as presented in this article is organized in the following manner. Firstly, 134 135 in the introduction section, the general background and the aim of this work are presented. After the introduction, the numerical model as developed in the present work is discussed 136 137 including the mathematical formulation of the heat and mass transport equations employed in the TCM bed, the computational procedure, and the model validation. Further, the results of 138 the numerical simulations and a parametric study for the hydration of the TCM bed are 139 analyzed. Finally, a summary along with the key conclusions of the present work is presented 140 141 in the last section.

142 2. GEOMETRY AND MODEL IMPLEMENTATION

The working pair of the material considered in the present study is potassium carbonate and 143 water vapor. Olives and Mauran [40] showed that heat transfer in TCM bed through thermal 144 radiation can be ignored as the working temperature of the thermochemical heat storage 145 system considered here is in the range of 10 °C to 90 °C only. They further showed that, for a 146 system with water vapor, the prevailing heat transfer mode is conduction. Heat transfer by 147 convection in the porous medium can also be neglected as the reaction between the potassium 148 149 carbonate and the water vapor is supposed to be instantaneous and gets completed so fast that there is no temperature difference between the salt and the water vapor and single 150 151 temperature equations can be used for the macroscopic description of the heat transfer processes in the porous medium. The vapor transport in the TCM can be of Knudsen, Darcy, 152 or inertial flow type since it depends on vapor pressure and velocity at the porous media 153 boundaries. The fluid is considered to flow through the TCM bed consisting of approximately 154 spherical particles with global porosity. Water vapor is considered an ideal gas, due to its low 155 concentration and partial pressure. A relatively low permeability value of the porous bed 156 (Table 1) makes it possible to model mass transfer with Darcy's law. The sensible heat of the 157 reactive bed is also taken into account in the energy balance considering the sensible heat of 158 159 water vapor and the stored heat in the salt as one entity. We also assume that the thermal 160 conductivity and heat capacity of the salt are constants. The thermo-physical properties of potassium carbonate, water vapor, and operating parameters that have been used in the model 161 162 are given in Table 1. The following assumptions have been made in the present study: (i) the properties of the phases are isotropic and uniform. Unless specified otherwise the physical 163 164 and chemical properties of the constituents are assumed to be constant; (ii) the water vapor is in thermal equilibrium with the solid phase; (iii) The porous medium is not deformable; (iv) 165 166 The gaseous adsorbate adheres to the ideal gas law; (v) The effects of pressure work and 167 viscous dissipation are negligible.

Table 1. The thermophysical properties of TCM and operating parameters considered in the present study [22,41]

Name	Value	Description
d_p	$0.5 \times 10^{-3}m$	particle diameter
E _{eff}	0.4	effective bed porosity
D_{v}	$10^{-9} m^2/s$	water vapor diffusion coefficient
$C_{p,v}$	1864 J/kgK	heat capacity of water vapor

C _{p,s}	830 J/kg K	heat capacity of solid potassium carbonate
$C_{p,fin}$	900 J/kg K	heat capacity of fin material
ρ_{s}	2210 kg/m ³	the density of potassium carbonate
ρ_{fin}	2700 kg/m ³	density of fin
k _{eff}	0.44 W/m K	thermal conductivity of potassium carbonate
k _{fin}	238 W/m K	thermal conductivity of fin
Ea	46.22 kJ/mol	activation energy
M_v	0.01802 kg/mol	the molar mass of water vapor
M _s	0.138 kg/mol	the molar mass of $K_2 CO_3$
χ	1.5	stoichiometric coefficient
ΔH_r	64.01 kJ/mol	reaction enthalpy kJ/mol of water
R	8.314 J/mol K	ideal gas constant
A_f	$3.0838 \times 10^{6} 1/min$	pre-exponential factor in reaction kinetics
T _i	30° <i>C</i>	initial temperature
T _{eva}	15°C	evaporator temperature
T_{HTF}	30° <i>C</i>	cooling temperature of HTF
p _i	425 Pa	initial pressure
C _i	0.07 mol/m ³	initial concentration

The schematic of the honeycomb heat exchanger thermochemical reactor bed considered in 168 the present study is illustrated in Fig. 1A. The system consists of several honeycomb heat 169 exchanger beds filled with K_2CO_3 particles and separated at a distance to allow water vapor 170 to reach the TCM material. The thickness of each honeycomb heat exchanger bed is indicated 171 with δ_b . The heat transfer fluid (HTF) tubes are connected in the center to each heat 172 exchanger unit in the system. The whole system is enclosed in a chamber where water vapor 173 is injected from the evaporator and relatively cold water is flowing in the HTF tubes. An 174 expanded side view of one honeycomb heat exchanger is presented in Fig. 1B, where 175 hexagonal cells are connected to HTF tubes and the distance between two HTF tubes is given 176 by $t_{gap,HTF}$. Further, the HTF tubes are arranged in such a way that they make a hexagonal 177 178 pattern themselves. Because of the hexagonal pattern of the HTF tube distribution in each honeycomb heat exchanger bed, symmetry can be considered in the heat and mass transport 179 180 processes. Due to this symmetry in heat and mass transport, a small element of the reactor

181 bed is considered in the present study (red dashed line in Fig. 1B). A three dimensional schematic of the computational domain is presented in Fig. 1C, where L_c is one edge of the 182 hexagonal cell, δ_{fin} is the thickness of the hexagonal cell wall and R_{tube} is the radius of the 183 HTF tube. The height of the computational domain is considered as half of the bed height 184 because of the presence of symmetry in the heat and mass transfer at the center of each 185 honeycomb heat exchanger bed as water vapor is transported from both sides of the bed. It is 186 noted here with reference to Fig. 1C that the numerical simulations are carried out in a 187 Cartesian coordinate system x, y and z because the system is not exactly cylindrical. 188 However, the x-coordinate more or less corresponds to the radial position and the y-189 coordinate to the tangential position. 190

In the present study, the radius of the HTF tube is constant for all the cases and its value is 191 192 taken 0.02 m. It is also assumed that the temperature gradient in the HTF flow direction is very small and can be neglected. The temperature at the internal surface of the HTF tube is 193 set equal to the inlet temperature of HTF and its value is 30 °C. The inlet of water vapor is 194 considered at the top of the computational domain and the symmetry boundary at the bottom 195 of the computational domain. At the top of the computational domain, the water vapor arrives 196 with a fixed vapor concentration of 0.71 mol/m^3 . This value is obtained based on water 197 vapor properties as it is assumed that vapor is an ideal gas (hence we applied the gas law 198 formula $\rho_v = M_v C$). The vacuum in the whole system is created at a pressure of around 1708 199 Pa. At t = 0, the concentration in the TCM bed equals 0.07 mol/m³ and the initial temperature 200 201 is set to 30 °C.



202

Fig. 1 Schematic of the geometry of the TCM bed and computational domain (a)
 TCM energy storage system, (b) side view of honeycomb heat exchanger filled with
 TCM, (c) computational domain.

206 **3. GOVERNING EQUATIONS**

207 3.1 VAPOR TRANSPORT IN POROUS MEDIUM

The vapor transport in the TCM filled in the honeycomb cells is governed by the mass conservation equation of the reactive gas and can be written as [42]:

210
$$\varepsilon_{eff} \frac{\partial C}{\partial t} - \nabla \cdot (D_v \nabla C) + \nabla \cdot (\boldsymbol{u}C) - R_C = 0$$
(1)

where C and D_{v} are the concentration and the diffusion coefficient of the water vapor, 211 respectively. ε_{eff} is the effective porosity and its value is taken 0.4 in the present study [41]. 212 The last term (R_c) in eq. (1) is the reaction term which will be discussed in the reaction 213 214 kinetics section. The vapor transport in the porous medium occurs not only from diffusion but also from advection, where a difference in pressure causes the bulk motion of the gas. This 215 leads to a viscous flow and therefore the vapor transport in the porous medium is governed by 216 Darcy's law considering the acceleration due to gravity. The Darcy velocity \boldsymbol{u} in the porous 217 medium is given by: 218

219
$$\boldsymbol{u} = -\frac{\kappa}{\mu} (\nabla p - \rho_{\nu} \vec{g})$$
(2)

where ρ_v is water vapor density and g is universal gravitational constant. The p is the gas pressure and given by gas law (p = CRT, where C is the molar concentration, R is the universal gas constant and T is the temperature). The permeability κ of the porous medium can be obtained from the semi-empirical Blake–Kozeny equation as:

224
$$\kappa = \frac{d_p^2 \varepsilon_{eff}^2}{150(1 - \varepsilon_{eff})^2}$$
(3)

where d_p is the particle diameter and ε_{eff} is the bed porosity. The Sutherland law or the viscosity-temperature relation is often used to determine the dynamic viscosity μ in the range of -156 [°C] to 1787 [°C], where the ratio S/T_{ref} is empirically taken as 0.505 [43].

228
$$\mu = \mu_{ref} \left(\frac{T}{T_{ref}}\right)^{\frac{1}{2}} \left\{\frac{1 + \frac{S}{T_{ref}}}{1 + \frac{S/T_{ref}}{T/T_{ref}}}\right\}$$
(4)

229 with T_{ref} and μ_{ref} as reference temperature and viscosity respectively.

230 3.2. HEAT TRANSFER IN POROUS MEDIUM

For the phases existing in the reactor bed, the macroscopic description of heat transfer in a porous medium is often investigated by the use of a single temperature equation. Here, local thermal equilibrium is referring to the fact that the macroscopic temperatures of the three phases (liquid water in the salt, water vapour in the reactive gas and the solid salt itself) are close enough such that a single temperature description of the heat transport processes can be used. Duval et al. [44] added that the assumption of local thermal equilibrium was acceptable
in many cases of unsaturated porous media with liquid–vapour phase change, particularly for
most thermal decomposition processes. Therefore the heat transfer in the porous
thermochemical bed is governed by the heat transfer diffusion equation, which can be written
as [42]:

241
$$\left(\rho C_p\right)_{eff} \frac{\partial T}{\partial t} + \rho_v C_{p,v} \boldsymbol{u} \cdot \nabla T - k_{eff} \nabla^2 T = Q$$
(5)

where $(\rho C_p)_{eff}$ is the effective volumetric heat capacity, k_{eff} is the effective thermal conductivity and its value is considered 0.4 W/mK in the present study [41]. The Q is the heat generated due to the reaction of water vapour with K_2CO_3 and its value depends on the reaction term R_c and will be discussed in the reaction kinetics section. The effective volumetric heat capacity $(\rho C_p)_{eff}$ is calculated by the following equation:

247
$$\left(\rho C_p\right)_{eff} = \rho_v C_{p,v} \varepsilon_{eff} + \rho_s C_{p,s} \left(1 - \varepsilon_{eff}\right)$$
(6)

248 3.3. HEAT TRANSFER IN FIN

249 The heat transfer in the fin can be calculated with the heat transfer diffusion equation [45]:

250
$$\rho_{fin}C_{p,fin}\frac{\partial T}{\partial t} - k_{fin}\nabla^2 T = 0$$
(7)

where ρ_{fin} , $C_{p,fin}$ and k_{fin} is the fin density, heat capacity and thermal conductivity respectively.

253 3.4. REACTION KINETICS

Solving the intra-particle mass balance equations is often time-consuming. To avoid this problem, in practice often a lumped approach is followed as an approximation, which has proven to be physically consistent [14,46]. The reaction term in equation (1) is calculated, using the reaction advancement:

258
$$R_c = \chi \, \frac{\rho_s}{M_s} \left(1 - \varepsilon_{eff} \right) \frac{\partial \alpha}{\partial t} \tag{8}$$

where ρ_s is the density of the solid TCM, χ is the Stoichiometric coefficient, M_s is the molecular weight of potassium carbonate and α is the reaction advancement. Since reaction kinetics deals with measurement and parameterization of the process rates, the rate can be parameterized using three major variables: the temperature T, the chemical conversion α and the vapor pressure *p*. Systematic studies have been performed about the different expressions of the kinetic rates [15] in heterogeneous kinetics and the global form of that rate can be presented as follows:

266
$$\frac{\partial \alpha}{\partial t} = k(T)f(\alpha)h(p) \tag{9}$$

The value of the conversion α in time-dependence reflects typically the progress of the overall transformation of a reactant to products, meaning the advancement of the reaction. Lu et al. [47] (1996), Mazet et al. [48] had shown that the pressure dependence for reversible solid-gas synthesis can be expressed as:

$$h(p) = 1 - \left(\frac{p_{eq}}{p}\right) \tag{10}$$

where *p* and p_{eq} are the partial and equilibrium pressures of the gas product respectively (here the water vapour). The value of equilibrium vapour pressure $p_{eq}[Pa]$ is given by [22]:

274
$$p_{eq} = 4.228 \times 10^{12} exp\left(-\frac{7337}{T}\right)$$
(11)

where T is the temperature in K. The ratio between equilibrium water vapor pressure (p_{eq}) and water vapour pressure (p) called the pressure ratio $(\frac{p_{eq}}{p})$, is an important parameter in reaction kinetics. Assuming that mass transfer and chemical reaction are sufficiently rapid so that equilibrium values of concentrations always exist at prevailing temperature, the equation linking the equilibrium pressure to the temperature for the decomposition is given by the Clausius-Clapeyron relationship. For this type of reaction, several authors [5,47,48] have shown that the reaction rate can be presented as follows:

282
$$\frac{\partial \alpha}{\partial t} = A_f exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^{2/3}\left(1-\frac{p_{eq}}{p}\right)$$
(12)

where A_f is the pre-exponential Arrhenius factor taking into account the kinetic effect, E_a the Arrhenius activation energy. The source term Q in the eq. (8) is the heat generated or consumed in adsorber bed which is given by:

$$Q = R_c \Delta H_r \tag{20}$$

where R_c is the reaction rate as introduced previously and ΔH_r is the reaction enthalpy (given in table 1).

289 3.5. INITIAL AND BOUNDARY CONDITIONS

- 290 The following boundary conditions are prescribed, see Fig. 1C:
- At the top of the computational domain, the water vapour pressure is fixed.
- At the bottom of the computational domain, the symmetry boundary condition is applied,
 for temperature and gas flux.
- At the surface of the honeycomb heat exchanger, the velocity field is zero $(-n\nabla u = 0)$,
- there are heat continuity between porous TCM and honeycomb fin, therefore

296
$$(-nk_{eff}\nabla T = -nk_{fin}\nabla T).$$

286

- At the HTF tube inner surface, a constant temperature boundary condition is applied ($T = T_{HTF}$).
- At the periphery (other than the HTF boundary) of the computational domain, the
 symmetry boundary condition is applied.

Initially, the temperature of the computational domain was $(T_i = 30^{\circ}C)$ and the reaction advancement of the bed is fixed at zero ($\alpha = 0$). The initial pressure is fixed at 425 Pa corresponding initial water vapor concentration is 0.07 mol/m³.

304 3.6. COMPUTATIONAL PROCEDURE AND MODEL VALIDATION

The governing partial differential equations subjected to initial and boundary conditions are simultaneously solved using the commercial package of COMSOL Multiphysics 5.3a, which is based on the Finite Element Method (FEM). The expressions for the thermophysical properties of TCM and reaction kinetics are programmed in COMSOL through user-defined functions. The partial differential equations for heat and mass transport are programmed in the 'heat transfer in porous media' and 'transport of diluted species in porous media'

interfaces available in COMSOL [49]. With respect to the 3-dimensional model for the heat 311 and mass transport study, free meshing with tetrahedral elements is used to create the overall 312 mesh. The numerical simulation model is divided into two calculation domains i.e. the solid 313 and the porous domain and each discretized using the Galerkin method. The mesh size and 314 time step dependencies of the solutions are studied to check the accuracy of the numerical 315 results and computation time. It was optimized with three progressive decreasing mesh sizes 316 317 and final values are taken because further reducing mesh size did not significantly affect the final results. The mesh size was decreased near the interfaces of the solid with the porous 318 319 medium to reduce the error in the calculations. The maximum and minimum mesh element size considered in the present study is 0.0013 m and 0.000132 m which is small enough to 320 obtain accurate mesh independent solutions. An independent discretization of the time 321 domain is applied using the method of lines and time-stepping algorithms automatically 322 switch between explicit and implicit steps depending on the problem. The time step may vary 323 in order and step length depending on the evolution of the solution with time. The maximum 324 time step is defined as 1 min, however, at the initial stage of convergence, the time step is 325 taken very small by the solver, in the order of 10^{-3} seconds. 326

327 The numerical model for heat and mass transport in the porous medium as used in the present study is based on a model developed in our lab for the hydration of silica gel. First, the 328 329 kinetics of silica gel is replaced with the kinetics of potassium carbonate, and then the heat transfer model for the honeycomb heat exchanger is added. The developed model for the 330 reaction kinetics is validated with experimental results presented by Gaeini et al. [22] in 331 terms of reaction advancement, see Fig. 2. In the experiments, the hydration isotherm is kept 332 at 30 °C and hydration starts only when water vapor is introduced to the system while the 333 isotherm temperature is maintained. The water vapor pressure was maintained at 1715 Pa. 334 335 More details can be found in Gaeini et al. [22]. The comparative results present the validity of the developed model as results from the present study are in good agreement with the 336 experimental results obtained by Gaeini et al. [22]. However, a minor shift compared to the 337 experimental data is observed. This can be explained by a possible difference in some 338 thermo-physical properties (effective thermal conductivity and effective porosity) of the 339 340 porous K₂CO₃ sample as these values are not presented by Gaeini et al. [22]. In the present work, these properties are taken from the literature [41]. 341



Fig. 2 Comparison of reaction advancement with experimental study of Gaeini et al. [22]

344 4. RESULTS AND DISCUSSION

The present study is conducted for the hydration of K_2CO_3 and the obtained results of the study are presented in two subsections. The initial and boundary conditions considered in the present study are listed in Table 1 and section 3.5. In the first subsection the heat transfer, reaction advancement and reaction rate are being discussed. In the second subsection, the results of the parametric study for different cell sizes (L_c), bed heights (δ_b), fin thickness (δ_{fin}) and the distance between two HTF tubes ($t_{HTF,gap}$) are discussed.

4.1. HEAT TRANSFER, REACTION ADVANCEMENT AND REACTION RATE

Figure 3 presents the temperature contour of the computational domain (i.e. TCM bed with 352 353 honeycomb heat exchanger) at 5 min, 15 min, 30 min, 60 min, 90 min and 120 min considering $L_c = 0.01 \, m$, $\delta_b/2 = 0.015 \, m$, $\delta_{fin} = 0.001 \, m$ and $t_{gap,HTF}/2 = 0.090 \, m$. 354 For the given configuration, the actual volume of the porous K_2CO_3 sample is 52.43 cm³ and 355 the ratio of the porous bed to fin volume is 3.6. From Figure 3, it can be observed that the 356 temperature in the computational domain for each time span is increasing with an increase in 357 the distance from the HTF tube and also increases towards the center of each hexagonal cell 358 359 of the honeycomb heat exchanger. Further, the temperature is higher at the top of the computational domain and starts decreasing with an increase in the distance from the top of 360 361 the bed as the concentration of the water vapour is progressively decreasing with an increase in the distance which results in a reduced heat generation in the bed. The temperature 362

distribution in each hexagonal cell is not perfectly symmetric; its maximum value is slightly
shifted away from the HTF tube. The temperature distribution in the y-direction of the bed
(comparable to the tangential direction in cylindrical coordinates) is almost periodic because
of symmetry in the hexagonal fin structure of the honeycomb.



367

Fig.3 Colour contour of the temperature of TCM bed at different time levels (a) 5 min, (b) 15
min, (c) 30 min, (d) 60 min, (e) 90 min, (f) 120 min

Further, the temperature variations with time at different probe points in the computational domain are shown in Fig. 4. The probe points P1 to P5 are equally spaced at a distance of 0.02 m in the x-direction (radial direction) starting from the HTF tube and P5 to P8 are positioned at the center of each hexagonal cell and also space at an equal distance of 0.01732 m in the y-direction (tangential direction) from probe point P5. Further, all the probe points are positioned at the half-thickness of the computational domain ($z = \delta_b/4$).





Fig. 4 Temperature variation at the different probe points (a) in the x-direction (radial
direction), (b) in the y-direction (tangential direction)

379 Fig. 4 shows the honeycomb heat exchanger bed temperature variation at the above-discussed probe points (i.e. P1 to P8). The temperature of the bed at all probe points is increasing 380 sharply at the initial stage of reaction and reaches its maximum value at around 10 min, 381 further it starts decreasing gradually. Fig. 4(a) represents the variation of bed temperature 382 with time at probe point P1 to P5. The minimum temperature is observed at probe point P1 as 383 it is nearest to the HTF tube. The temperature of the bed is increasing with an increase in 384 distance from the HTF tube, though, the temperature at probe point 4 is lower than P3 as P4 385 is positioned in the honeycomb fin and P3 is placed in the center of the hexagonal cell. Fig 386 4(b) represents the variation of temperature at different probe points (P5 to P8) in the y-387 direction (tangential direction). The temperature difference in probe points P5 to P8 is very 388 389 small because of the presence of the honeycomb fin structure and symmetry considerations.

390

Fig 5 presents the variation of reaction advancement (α , eq. (12)) and reaction rate (R_c , Eq. (8)) of water vapor with K_2CO_3 at different probe points with time. The positions of probe

393 points are presented above. Because the probe points P2 and P4 coincide with the fin structure, they are left out of this analysis. Up to 55 min, the reaction advancement is the 394 highest at probe point P1, from 55 min onwards probe point P3 shows the highest reaction 395 advancement, as shown in Fig. 5(a). Minimum reaction advancement is obtained at probe 396 point P8 because it is the furthest probe point from the HTF tube in the thermochemical 397 reactor bed. The decreasing order of reaction advancement at different probe points before 398 399 and after 55 min is P1>P3>P5>P6>P7>P8 and P3>P1>P5>P6>P7>P8 respectively. It should be noted however that the values for reaction advancement are quite close to each other for 400 401 the points P5-P8 over the full-time interval. This applies to all points for times greater than 80 min. Besides, the reaction rate of water vapour with K_2CO_3 at the different probe, points are 402 shown in Fig. 5(b). Initially, the reaction rate increases sharply and reaches its maximum 403 value for all probe points and then it starts decreasing with different proportions. At probe 404 point P1, the reaction rate continuously decreases after getting its maximum value, though, 405 406 for other probe points, the reaction rate sharply decreases with time until reaches its minimum value (\approx t = 10 min). After reaching the minimum value of reaction rate it further 407 408 starts increasing with time up to \approx 35 min for P3 and t = \approx 55 min for P5, P6, P7, P8. This can be explained as the water vapour seeps into the bed and reacts with TCM, which results in the 409 410 temperature rise in the bed. The temperature rise in the bed causes a reduction in the reaction 411 rate.





414

Fig. 5 Variation of (a) reaction advancement, (b) Reaction rate at the different probe points with time

415 4.2. PARAMETRIC STUDY

Below a discussion on the results obtained from a parametric study of honeycomb cell size, bed height, honeycomb fin thickness and the distance between two HTF tubes are presented. The results are presented in terms of temperature variation (T), reaction advancement (α) and power output (P_o). The power output P_o is obtained by integrating the heat flux over the HTF tube surface and is defined as:

421
$$P_{o} = \oiint \vec{q} \, dS$$

422 with the heat flux \vec{q} integrated over the surface *S* of the HTF tube.

423 4.2.1. Effect of honeycomb cell size

Fig. 6 shows the temperature contours of the computational domain for four different 424 425 honeycomb cell sizes i.e. $L_c = 0.005$ m, 0.01 m, 0.015 m, and 0.02 m at 15 min. The default values of $\delta_b/2$, δ_{fin} and $t_{gap,HTF}/2$ for all the cell sizes are 0.015 m, 0.001 m, and 0.09 426 respectively. The volumes of the porous K_2CO_3 samples for $L_c = 0.005$ m, 0.01 m, 0.015 m, 427 and 0.02 m are 52.43 cm^3 , 59.49 cm^3 , 61.95 cm^3 and 63.20 cm^3 respectively. Further, the 428 volume ratios of the porous K₂CO₃ samples with respect to the metallic fin volumes are 3.6, 429 7.9, 12.25 and 16.57 respectively. The smaller honeycomb cell size increases the number of 430 cells in the TCM bed and consequently also increases the fin material volume. The increment 431 of the fin volume in the computational domain causes enhanced heat transport in the bed; 432 however, it reduced the actual heat capacity of the bed. The temperature gradient in the 433 computational domain is lowest for the smallest cell size of the honeycomb structure and vice 434 435 versa, because of better heat transport from the TCM bed to the HTF.



436

437 Fig. 6 Temperature contours at different cell sizes (a) $L_c = 0.005$ m, (b) $L_c = 0.01$ m, (c) $L_c =$ 438 0.015 m, (d) $L_c = 0.02$ m at 15 min

Further, the temperature variation, reaction advancement and thermal power transported to
the HTF with time are plotted in Fig. 7 at probe point 8 (as shown in fig 5a). The temperature
at probe point P8 (the point furthest away from the HTF tube) increases sharply for all the

443 cell sizes and gradually starts decreasing after reaching its maximum value as shown in Fig 7(a). For the lowest cell size ($L_c = 0.005$ m), the maximum temperature at probe point P8 444 reaches 47 °C after 10 min. Further, the temperature gradually starts decreasing and reaches 445 the lowest value of 32 °C at 120 min. For $L_C = 0.01$ m, the temperature at probe point P8 446 sharply reaches its maximum value and starts decreasing gradually until 60 min. Further, it 447 sharply decreases and becomes 32 °C after 120 min. Fig. 7(b) shows the reaction 448 advancement at probe point P8 for all cell sizes. For $L_c = 0.005$ m and $L_c = 0.01$ m, the 449 reaction advancement at 120 min reaches around 0.95 however for $L_c = 0.015$ m and $L_c =$ 450 451 0.02 m its value is 0.8 and 0.35 respectively.



Fig. 7 Variation of (a) Temperature, (b) reaction advancement and (c) power output with time
for different cell sizes; temperature and reaction advancement are presented for probe point

P8

455

The lowest reaction advancement is obtained with the highest cell size because of the higher 456 temperature which causes a reduced reaction rate of water vapour with K_2CO_3 . Fig. 7 (c) 457 presents the variation of power output with time at the HTF tube surface in the computational 458 domain. The power output (P_0) reaches its maximum value at the same time when the 459 temperature at probe point P8 is maximum. For $L_c = 0.015$ m and $L_c = 0.02$ m, there is a 460 gradual reduction in power output after reaching its maximum value, however, it is sharper 461 for $L_c = 0.005$ m and $L_c = 0.01$ m. The smaller honeycomb cell size leads to a higher number 462 of cells in the computational domain which reduces the actual volume of the reacting material 463 in the computational domain. The reduction in the volume of reacting material reduces the 464 heat storage capacity of the reacting bed. 465

466 4.2.2. Effect of bed height

467 The temperature contours of the computational domain for four different bed height ($\delta_b/2 =$ $0.005 \ m, \ \delta_b/2 = 0.01 \ m, \ \delta_b/2 = 0.015 \ m, \ \text{and} \ \delta_b/2 = 0.02 \ m)$ at 15 min are presented in 468 Fig. 8. The fin thickness, honeycomb cell size and the distance between two HTF tubes are 469 470 considered 0.001 m, 0.01m and 0.09 m respectively. The volumes of the porous K₂CO₃ samples for $\delta_b/2 = 0.005 m$, $\delta_b/2 = 0.01 m$, $\delta_b/2 = 0.015 m$, and $\delta_b/2 = 0.02 m$ are 471 19.83 cm^3 , 39.66 cm^3 , 59.49 cm^3 and 79.32 cm^3 respectively. The ratio of the porous 472 K₂CO₃ sample volume to the metallic fin volume is fixed at 7.9. At 15 min, the temperature 473 gradient in the computational domain is almost the same for all bed heights (Fig. 8 (a)-(d)), 474 however, its value is slightly higher for the computational domain with the lowest bed height 475 as compared to the higher bed height (Fig. 9). For the smaller bed height, the water vapour 476 easily seeps into the bed and reacts with the TCM, which enhances the reaction rate and 477 results in a higher temperature. 478





481 Fig. 8 Temperature contours at different bed height (a) $\delta_b/2 = 0.005 m$, (b) $\delta_b/2 = 0.01 m$, 482 (c) $\delta_b/2 = 0.015 m$, (d) $\delta_b/2 = 0.02 m$ at t=15 min



486

Fig. 9 Variation of (a) Temperature, (b) reaction advancement and (c) power output with time
for different cell sizes; temperature and reaction advancement are presented for probe point

P8

The temperature at probe point P8 (discussed in the previous section) is presented in Fig 9 (a) for different bed thicknesses. At this probe point the bed temperature is higher for the lowest bed thickness until t = 60 min and vice versa after 60 min. Further, reaction advancement is always higher for the lowest bed height (i.e. $\delta_b/2 = 0.005 m$) because of the lower flow resistance and lower uptake of vapor in the bed which results in better accessibility of and higher concentration in the computational domain. Further, the power output from the 493 computational domain to the HTF surface is presented in Fig. 9(c). The maximum power is obtained with the maximum bed thickness simply because of the presence of more TCM in 494 the computational domain. However, it is interesting to see that the power output is linearly 495 increasing with the bed height for the 2 smaller values ($\delta_b/2 = 0.005 m$ and $\delta_b/2 =$ 496 0.01 m) but slightly decreases for the 2 larger values ($\delta_b/2 = 0.015 m$ and $\delta_b/2 = 0.02 m$). 497 There is a progressive attenuation in power with time for higher bed height because the 498 fraction of hydrated TCM increases and subsequently reduce the reactant volume with time, 499 500 which results in lower production.

501

502 4.2.3. Effect of honeycomb fin thickness

The temperature variation of the computational domain for four different fin thicknesses 503 $(\delta_{fin} = 0.0005 \, m, \, \delta_{fin} = 0.001 \, m, \, \delta_{fin} = 0.0015 \, m, \text{ and } \delta_{fin} = 0.002 \, m)$ at 15 min are 504 presented in Fig. 10 considering $L_c = 0.01$ m, $\delta_b/2 = 0.015$ m and T _{gap.HTF}/2 = 0.09 m. 505 The volumes of the porous K2CO3 samples for $\delta_{fin} = 0.0005 m$, $\delta_{fin} = 0.001 m$, $\delta_{fin} =$ 506 0.0015 m, and $\delta_{fin} = 0.002 m$ are 63.19 cm³, 59.49 cm³, 55.90 cm³ and 52.43 cm³ 507 respectively. Further, the ratios of the porous K2CO3 sample volumes to the metallic fin 508 volumes are 16.57, 7.92, 5.03 and 3.60 respectively. The highest temperature gradient in the 509 TCM bed is observed with the lowest fin thickness due to the reduction in the thermal 510 transport from the bed to the HTF surface (increased heat resistance because of a reduced 511 cross-sectional area of the fin structure). Further, the increment in the fin thickness also 512 reduces the actual volume of the TCM in the bed, which also results in reduced heat 513 514 generation and causes a lower bed temperature.





Fig. 10 Temperature contours at different honeycomb fin thickness (a) $\delta_{fin} = 0.0005 m$, (b) $\delta_{fin} = 0.001 m$, (c) $\delta_{fin} = 0.0015 m$, (d) $\delta_{fin} = 0.002 m$ at t=15 min



Fig. 11 Variation of (a) Temperature, (b) reaction advancement and (c) power output with time for different cell sizes; temperature and reaction advancement are presented for probe point P8

Further, the temperature variation, reaction advancement at probe point P8 and power output 522 from the computational domain are presented in Fig 11 (a), Fig. 11(b) and Fig. 11 (c) 523 respectively. The temperature for the minimum fin thickness is the highest and, vice versa, 524 the temperature for the maximum fin thickness is the lowest which is understandable because 525 it influences the thermal transport from the bed to the HTF as discussed above. For $\delta_{fin} =$ 526 0.001 m, $\delta_{fin} = 0.0015$ m, and $\delta_{fin} = 0.002$ m the temperature at 120 min reaches to 32 527 °C, slightly above its initial value of 30 °C, however for $\delta_{fin} = 0.0005 m$ its value is still 528 around 59 °C because the hydration reaction is still in full swing as can be concluded from the 529 530 reaction advancement. The reaction advancement at probe point P8 is presented in Fig. 11 (b). From Fig. 11(b) it is observed that the reaction advancement reached around 0.98 at 120 531 min, for the fin thickness greater than 0.0005 m, however, it reaches 0.68 for fin thickness 532 0.0005 m. The power output from the TCM bed is presented in Fig. 11(c). Initially, the power 533 output sharply increases and starts decreasing gradually after reaching its peak value. The 534 535 maximum peak power is obtained for fin thickness $\delta_{fin} = 0.0015 m$, the minimum peak power for fin thickness of $\delta_{fin} = 0.0005 \ m$. In Fig. 11 (c) it is also observed that the power 536 output with $\delta_{fin} = 0.002 m$ fin thickness is lower as compared to $\delta_{fin} = 0.0015 m$ because 537 a larger fin thickness results in a larger volume of fin material and reduces the actual volume 538 539 of the TCM which causes lower power output. Finally, it is interesting to note that for a lower fin thickness the peak power goes down but the power is more constant over time than for a 540 541 higher fin thickness.

542 4.2.4. Effect of distance between two HTF heat pipe

Numerical simulations have also been conducted to see the effect of the distance between two 543 HTF tube $(t_{qap,HTF})$. The simulations have been performed for $t_{qap,HTF}/2 = 0.045 m$, 544 $t_{gap,HTF}/2 = 0.090 m$, and $t_{gap,HTF}/2 = 0.135 m$. The volumes of the porous K₂CO₃ 545 samples for $t_{gap,HTF}/2 = 0.045 m$, $t_{gap,HTF}/2 = 0.090 m$, and $t_{gap,HTF}/2 = 0.135 m$ are 546 12.78 cm³ 59.49 cm³ and 137.34 cm³ respectively and the ratio of the porous K₂CO₃ samples 547 to the metallic fins volume is fixed at 7.92. The obtained temperature contours at 15 min are 548 549 presented in Fig. 12(a), Fig. 12(b) and Fig. 12(c) respectively. The temperature gradient near the HTF tube in the computational domain is smaller for a smaller distance between two HTF 550 tubes. The temperature gradient in each cell near the HTF tube is also higher for the 551 higher $t_{gap,HTF}/2$. For maximum $t_{gap,HTF}/2$, when moving away from the HTF tube the 552

temperature gradient in each cell starts decreasing. At the maximum distance from the HTF 553 tube, the temperature gradient is negligible. Further, temperature variation and reaction 554 advancement at probe point 8 and power output from the TCM bed is presented in Fig 13(a), 555 Fig. 13(b) and Fig. 13(c) respectively. It is evident that for higher values of $t_{gap,HTF}/2$ the 556 temperature at probe point 8 is the highest. For $t_{gap,HTF}/2 = 0.045$ m and 0.09m, the 557 temperature increases to its maximum value and then it starts decreasing. For minimum 558 $t_{gap,HTF}/2$ (0.045 m), the maximum temperature reaches 37.5 °C at around 5 min and starts 559 decreasing gradually with time and reaches 31 °C at 120 min. For maximum $t_{gap,HTF}/2$ 560 (0.135 m), the temperature reaches 68 °C at 10 min and its value remains around 68 °C over 561 the whole time span. From the reaction advancement as presented in Fig. 13(b), it is observed 562 that the reaction advancement is higher for the lowest $t_{gap,HTF}/2$ in the initial stage of 563 reaction and becomes maximum for $t_{gap,HTF}/2 = 0.09 m$ after 60 min. Further, the power 564 output of the TCM bed is also presented in Fig. 13 (c) for different $t_{gap,HTF}/2$ values. For all 565 its values the power output increases in precisely the same way. However, the smaller the 566 $t_{qap,HTF}/2$ value, the earlier the maximum is reached. The maximum power output is 567 achieved with the highest $t_{gap,HTF}/2$ because of the higher volume of the TCM bed. 568





Fig. 12 Temperature contours for different distance values between two HTF tubes

572 (a) $\frac{t_{gap,HTF}}{2} = 0.045 \ m$, (b) $\frac{t_{gap,HTF}}{2} = 0.090 \ m$, (c) $\frac{t_{gap,HTF}}{2} = 0.135 \ m$ at t=15 min



Fig. 13 Variation of (a) Temperature, (b) reaction advancement and (c) power output with
time for different distances between two HTF tubes; temperature and reaction advancement
are presented for probe point P8

577 **5. CONCLUSIONS**

578 A thermochemical energy storage system using potassium carbonate and water as the 579 sorbent/sorbate reaction pair (K_2CO_3/K_2CO_3 . 1.5 H_2O) is studied numerically considering a 580 three-dimensional fixed honeycomb heat exchanger bed filled with K_2CO_3 -particles. The 581 thermochemical bed is cooled from the center of the honeycomb heat exchanger by an HTF flow. The developed numerical model for the reaction kinetics of potassium carbonate is 582 validated with experimental data in terms of reaction advancement. The results obtained 583 provide detailed insight into the temperature variation and reaction propagation in the 584 reactive solid TCM bed during discharging. A parametric study has been conducted to see the 585 effect on the heat transfer of the honeycomb cell size, the bed height, the honeycomb fin 586 587 thickness and the distance between two HTF tubes. It is concluded that an increase in bed height, cell size and fin thickness affect the discharge process to a great extent. Increasing the 588 height of the bed will restrict the vapor flow within the bed whereas increasing the cell size 589 590 and decreasing the fin thickness of the honeycomb heat exchanger will reduce the heat 591 transfer to/from the bed due to poor conductivity properties. Increasing the distance between 592 two HTF tubes will result in an increase of the temperature maximum and, therefore, will require heat transfer enhancement techniques if this temperature must remain below a certain 593 value (to avoid dehydration during hydration for example). 594

595 It can be concluded that the developed numerical model is a very powerful tool in predicting all details of the physical phenomena taking place in the three-dimensional fixed honeycomb 596 597 heat exchanger bed packed with K_2CO_3 -particles. The model is also well suited for other applications utilizing different TCMs and different heat exchanger configurations. Changes in 598 temperature, reaction advancement and power output with respect to geometry can easily be 599 investigated using a similar approach. The next step is the design and the test of a prototype 600 601 of the most optimal storage system equipped with honeycomb heat exchangers at a 602 significant scale. The test of this prototype will allow us to demonstrate the feasibility of the potassium carbonate seasonal thermochemical storage process with a fixed bed honeycomb 603 604 heat exchanger configuration functioning with water vapor for the built environment.

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