- 1 Salt impregnated desiccant matrices for 'open' thermochemical energy conversion and
- 2 storage Improving energy density utilisation through hygrodynamic &
- 3 thermodynamic reactor design.
- 4
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#### 15 Abstract

In this study, the performance of three nano-composite energy storage absorbents; Vermiculite-CaCl<sub>2</sub> (SIM-3a), Vermiculite-CaCl<sub>2</sub>-LiNO<sub>3</sub> (SIM-3f), and the desiccant Zeolite 13X were experimentally investigated for suitability to domestic scale thermal energy storage. A novel 3kWh open thermochemical reactor consisting of new meshed tube air diffusers was built to experimentally examine performance. The results were compared to those obtained using a previously developed flatbed experimental reactor.

SIM-3a has the best cyclic behaviour and thermal performance. It was found that 0,01 m<sup>3</sup> of SIM-3a can provide an average temperature lift of room air,  $\Delta T = 20$  °C over 180 minutes whereas for SIM-3f,  $\Delta T < 15$  °C was achieved. Zeolite provided high sorption heat in close approximation with SIM-3a, however, the higher desorption temperature requirements coupled with poor cyclic ability remain as obstacles to the roll out this material commercially.

27 The study results clearly show that the concept of using perforated tubes embedded inside the 28 heat storage material significantly improves performance by enhancing the contact surface area 29 between air  $\rightarrow$  absorbent whilst increasing vapour diffusion. The results suggest a linear 30 correlation between thermal performance and moisture uptake,  $\Delta T - \Delta w$ . Determining these

31	operating lines will prove useful for predicting achievable temperature lift and also for effective										
32	design and co	ntrol of thermochemical heat storage systems.									
33											
34	Keywords:										
35	Salt In Matrix	; Open Thermal Energy Storage; Vermiculite; Hygr	othermal, Thermochemical								
36											
37	Nomenclatur	re									
38	$C_D$	specific heat at constant pressure	J/(kg.K)								
39	c r	temperature gradient	°C/min								
40	d	diameter	mm								
41	$E_d$	energy density	$kJ/kg, kWh/m^3$								
42	$E_{cum}$	cumulative thermal energy	Wh, kWh								
43	Ex	exergy	W, kW								
44	Excum	cumulative thermal exergy	Wh. kWh								
45	H	Enthalpy	kJ/s								
46	т	mass	g, kg								
47	ma	mass flow rate of air	kg/s								
48	0	thermal power	W. kW								
49	~ RH	relative humidity	%								
50	$P_{v}$	partial vapour pressure	mbar								
51	S	entropy	kJ/kg								
52	t <sub>dwell</sub>	time interval to reach ambient temperature	hr								
53	t	time	s, hr								
54	Т	temperature	°C, K								
55	V	volume	m <sup>3</sup>								
56	W	absolute humidity	g/kg								
57	ρ	density	$kg/m^3$								
58	f	mass uptake ratio	$g_{\rm wv}/g_{\rm abs}$								
59	$\Delta$	difference									
60	<u> </u>	1 <sup>st</sup> law efficiency									
61	η η	$2^{nd}$ law efficiency									
62	'/"										
63											
64											
65	Subscripts										
66	tr	transferred									
67	dr	discharging									
68	cr	charging									
69	g	gain									
70	cum	cumulative									
71	abs	absorbent									
72	а	air									

73	WV	water vapour
74	W	wet
75	in	inlet
76	out	outlet
77	d	dry
78	avg	average
79	f	fan
80	h	heating
81	rxn	reaction
82	max	maximum
83	g	gain
84		
85		
86		
87		

#### 88 **1.** Introduction

Energy technologies and management strategies have been gaining more attention in the last 89 decade as energy is vital for a safer and sustainable future. Dependency on secure energy is 90 much higher than in the past due to growth in the industrial sector, increasing population as 91 well as comfort demands. According to Berners-Lee & Clarke, 2013, if global warming is not 92 93 to exceed 2 °C then only 20 % of the worlds established fossil fuel reserves can be burned by 2050 then this energy dependency represents a major threat to the future of all humans [1]. At 94 the current rate of fossil consumption however, it is predicted that this 2 °C rise will be achieved 95 by the year 2030 [1]. 96

In the built environment, the domestic building sector currently represents the highest energy 97 consumption as more people around the world aspire to better comfort living standards, driving 98 the demand for air conditioning and thus electrical energy [2]. Urgent energy management 99 solutions are required to increase the share of renewable sources for this comfort energy thus 100 reducing the over reliance on fossil fuel driven systems [3]. Within this context, various 101 international agreements such as the Kyoto Protocol seek to address this problem [4]. In 102 103 addition, the EU commission aims to increase the share of renewables to 20 % by 2020 in member countries [5, 6]. The IEO 2007 report states that domestic buildings are responsible for 104 40% primary energy consumption, 70% of electricity consumption and 40% of atmospheric 105 106 emissions in developed countries [7, 8]. Additionally heating, cooling and air conditioning (HVAC) and domestic hot water (DWC) constitute more than half of the energy consumption 107 in buildings [9]. 108

Solar energy is counted as one of the primary renewable energy sources and it has promising
potential for thermal applications (both space & water heating) in the domestic building sector.
However, the mismatch between solar availability and building heat demand constitutes a major
obstacle in residential applications usually resulting in the need for auxiliary systems / energy

sources such as heat pumps, electrical resistance heaters or gas heaters coupled with ever more 113 114 sophisticated energy management systems. Although the combination of multiple systems (*i.e.* hybrid systems) enables higher energy utilisation, it also increases the complexity, capital and 115 116 operational costs of these systems [10]. Heat storage systems can considerably improve the utility of solar thermal systems by acting as a 'thermal battery' by either thermo-physically or 117 118 thermo-chemically storing energy for later usage. Thermophysical systems are based on either 119 sensible heat storage (SHS) or latent heat storage (LHS) whilst thermochemical systems are 120 based on thermochemical heat storage (THS) [11]. All these systems can allow for conversion of solar energy for either short or long term storage, dependant on system type and material 121 122 used. Although both SHS and LHS systems have been widely researched in the past [12] and are somewhat mature technologies, THS is a relatively new technology for converting and 123 storing heat with much research ongoing on these systems. Caliskan et al. [13] performed 124 energetic, exergetic and sustainability assessments for SHS, LHS and THS. Researchers found 125 the effectivness of three different storage methods was in the order of SHS>THS>LHS in terms 126 127 of energetic and exergetic efficiency. However the main drawback of SHS compared with other storage methods is the low  $E_d$ . THS materials are gaining attention over the last decade due to 128 their high theoretical  $E_d$  and long term heat storage potential. In this context, Henninger et al. 129 [14] reviewed new materials for adsorptive heat transformation and storage. Similarly, Aristov 130 [15] investigated the current trends in dynamic optimization of adsorption heat storage. An 131 overview on sorption materials and technologies for heat pumps and thermal energy storage 132 applications was presented by Cabeza et al. [16]. In a recent study, Scapino et al. [17] 133 134 investigated the latest advancements at material and prototype scale for long term sorption heat 135 storage. A literature survey on adsorption thermal energy storage processes for heating applications was presented by Lefebvre and Tezel [18]. Schreiber et al. [19] experimentally 136 investigated a Zeolite based adsorption heat storage and demonstrated that heat losses have a 137 138 major impact on adsorption heat storage performance, particularly in long term applications.

Gaeini et al. [20] developed a model for predicting the thermal dynamics of a Zeolite based 139 adsorption bed concluding that the this could be useful for design and optimization of THS 140 systems. Michel et al. [21] developed a large scale sorption reactor consisting of multiple 141 142 sorption beds and air flow channels using Strontium bromide / water (SrBr<sub>2</sub> / H<sub>2</sub>O) as a reactive pair. A novel "revolving drum" reactor prototype was investigated by Zettl et al. [22]. Likewise, 143 144 a composite sorption reactor consisting of CaCl<sub>2</sub> impregnated mesoporous ceramic (Wakkanai siliceous shale) honeycomb filter was developed by Liu et al. [23] for low-temperature (< 145 100 °C) industrial waste heat recovery. Zhang et al. [24] experimentally investigated the 146 performance of a 10 kWh absorption thermal energy storage prototype using LiBr-H2O. 147 148 Energy storage densities for cooling, hot water and heating were found 42, 88 and 110 kWh/m<sup>3</sup>. Lele et al, [25] investigated a closed THS system operating with SrBr<sub>2</sub>.6H<sub>2</sub>O, as an addition to 149 cogeneration systems for storing process waste heat with a theoretical reactor  $E_d$  of 115 150 kWh/m<sup>3</sup>, storage capacity of 61 kWh and thermal efficiency of 78%. In another study, Jiang et 151 al [26] developed and experimented a sorption energy store for industrial heat recovery 152 153 applications. The  $E_d$  was found in the range of 596-662 kJ/kg where energy and exergy efficiencies varied between 27.5-40.6% and 32.5-47%, respectively. Hamdan et al. [27] 154 performed a parametric study on the potential of storing thermal energy with thermochemical 155 heat pump using water - sodium chloride as sorbate - sorbent couple. Fernandes et al. [28] 156 developed a dynamic model for investigating an adsorption heat storage unit (using silica 157 gel/water pair) integrated with a solar water heating system. The results revealed that adsorption 158 heat storage provides up to 16% savings in annual backup energy when compared with a similar 159 160 conventional storage system. In a recent study, a novel sorption heat pipe that utilizes composite 161 sorbent-sorbate (NaBr-NH<sub>3</sub>) as working media was developed by Yu et al. [29]. In another experimental study performed by Tatsidjodoung et al. [30], it was found that an open sorption 162 reactor loaded with 40 kg of zeolite can supply a constant power of 2.25 kW over two hours 163 corresponding to 27.5 W kg<sup>-1</sup> of material. Abedin and Rosen [31] investigated both closed and 164

open THS systems using energy and exergy analysis methods to evaluate the charging behavior 165 and overall cycle performance. Balasubramanian et al. [32] developed a mathematical model to 166 investigate the capability of salt hydrates to store thermochemical energy during their 167 168 dissociation into anhydrous salts and water with an external heat supply. Researchers reported that the heat supplied for desorption is gradually absorbed by the anhydrous salt and results in 169 170 an increase of desorption duration with an associated increase of heat loss to the environment. 171 Li et al. [33] developed a composite block by impregnating BaCl inside the graphite powder pores for thermochemical conversion and storage of solar energy. In another experimental 172 study, Mette et al. [34] developed a highly efficient regeneration process for a THS system. A 173 174 zeolite based composite material was used as the absorbent. Stitou et al. [35] carried out an experimental investigation of a solar assisted THS system used for air conditioning in a pilot 175 plant for housing in France. Tanguy et al. [36] conducted a parametric study to evaluate the 176 impact of both the internal (air flow rate, heat exchanger pressure drop) and external conditions 177 (outdoor temperature) on the performance of a THS system. A prototype THS system is 178 179 developed by Zondag et al. [37] at the Energy Research Centre of The Netherlands. It is a packed bed sorption system which contains 0.017 m<sup>3</sup> of sorption material (MgCl<sub>2</sub>.H<sub>2</sub>O). They 180 reported that an effective storage density of  $0.5 \text{ GJ/m}^3$  was obtained from the system. 181

Previous studies on an 'open' THS system (i.e. using the building air as the heat transfer fluid 182 with no heat exchanger) were carried out by the authors and identified three candidate materials 183 with promising application to 'open' THS (SIM-3a, SIM-3f and Zeolite 13X). Feasibility and 184 applicability of open THS under different climate conditions were theoretically investigated 185 through technical, economic and environmental analyses [38-39]. A modular open sorption pipe 186 187 was also developed and tested by the authors for seasonal solar energy storage [40]. It was found that system has a total energy storage capacity of 25.5 kWh and energy storage density 188 of 290 kWh/m<sup>3</sup>. In another study, a custom designed test rig (Gen2) was developed to assess 189 the hygrothermal cyclic behaviour of both adsorption and thermochemical materials [41] 190

A new design THS system (Gen3) using perforated tubes to increase vapour diffusion to the 191 Salt-In-Matrix (SIM) composite absorbent material was developed with the experimental 192 results of the first phase of testing presented in this paper. The aim of this research was to 193 194 improve overall energy output using the same materials tested previously, through comparative analysis of the results achieved in both rigs and further analysis of system operating parameters 195 196 and the cyclic / hysteretic performance of the Gen3 rig. There are currently a very limited 197 number of experimental studies investigating 'open' THS systems suitable for domestic 198 building thermal energy provision in the existing literature and it is envisaged that this new concept may act as a model for future short/long term development of these systems. 199

### 200 **2.** Methodology

201 In previous work by the authors a range of candidate porous materials and salts capable of producing adequate exothermic thermochemical reactions for 'open' THS when hydrated were 202 selected from the literature. From these, a total of eight SIM composites were synthesised using 203 204 the Insipient Witness Technique (IWT) method [42]. These were SIM-2a, SIM-3a, SIM-3b, SIM-3c, SIM-3d, SIM-3e, SIM-4a and SIM-8a. The technique utilises a dry porous materials 205 natural liquid absorption capacity (*i.e.* capillarity) to fill the pore structure with a desired salt 206 solution. Whilst Vermiculite has a small level of potential sorption energy due to its high 207 specific surface area, in this case it is used strictly as a host matrix in the composite material 208 inhibiting deliquescence of the salt and preventing any salt leakage during the THS cycling 209 operations. Analysis of the energy density,  $E_d$  of the materials suggested that SIM-3b 210 (Vermiculite with MgSO<sub>4</sub>) had the highest  $E_d$  of all samples however as it has very limited 211 212 absorption potential this energy may not be available under standard working conditions. SIM-3a (Vermiculite with CaCl<sub>2</sub>) appeared to have excellent  $E_d$  coupled with good moisture uptake 213 and response time to moisture with TGA (Thermo gravimetric analysis) also suggesting 214 significant mass loss in the working range 30 < T < 140 °C. These findings suggested that SIM-215 3a appears to have very good potential for use in an 'open' THS system. 216

From hygrothermal cycling experiments carried out using the Gen2 rig [41], Zeolite 13X provided the highest temperature lift of all samples in the first cycle due to the high amount of vapour adsorption and fast reaction kinetics. Whilst the hysteretic performance of SIM-3a was minimal, Zeolite 13X showed a sharp drop from cycle one to cycle four. Zeolite 13X requires a high regeneration temperature (> 180 °C) with the lower regeneration temperature prerequisite for this research unable to provide adequate dehydration, however as it is used extensively in the literature it was decided to use it for comparative analysis for this work.

A new composite THS material SIM-3f was developed that combined SIM-3a and SIM-3d 224 (Vermiculite with CaCl<sub>2</sub> and LiNO<sub>3</sub>). In previous findings [42] SIM-3d was considered to be 225 of interest as it performed well across four charge/discharge cycles albeit with a maximum 226 temperature lift, T<sub>out, max</sub> much lower than SIM-3a which, on its own, would be too low to suit 227 an 'open' THS system. SIM-3d appeared to have a near horizontal slope during the cyclic test 228 (*i.e.* from maximum temperature to ambient,  $T_{out, max} \rightarrow T_{ambient}$ ) suggesting that the dwell time, 229  $t_{dwell}$  (*i.e.* time taken for  $T_{out} = T_{ambient}$ ) for SIM-3d may far exceed those of the other synthesised 230 materials. It was proposed that combination of SIM-3d with SIM-3a may prove beneficial and 231 therefore is also investigated here. 232

SIM-3f was prepared using equal volumes of saturated solution (50% - 50%) of each salt in separate containers to prepare the final mixed CaCl<sub>2</sub>-LiNO<sub>3</sub> solution before impregnation. The solubility of CaCl<sub>2</sub> and LiNO<sub>3</sub> at room temperature (20 °C) are 745 g/l and 522 gr/l with the molar weight at the same conditions being 110.98 g/mol and 68.95 g/mol respectively. Therefore the mass ratio of CaCl<sub>2</sub> / LiNO<sub>3</sub> impregnated to the host matrix (vermiculite) was calculated as 1.42 whereas molar ratio was 0.88.

Obtained Scanning Electron Microscopy (SEM) images of raw vermiculite, SIM-3a, SIM-3f and Zeolite 13X are presented in Figure 1. Vermiculite has a micro-scale lamellar structure, enabling salt impregnation inside the voids between lamellas (See: Figure 1A). In Figure 1B,

- solid crystals of CaCl<sub>2</sub> are clearly visual between the lamellas, whereas the LiNO<sub>3</sub>-CaCl<sub>2</sub>
- 243 mixture was coalesced within the lamellas acting more like a coating (See: Figure 1C).





Zeolite 13X has much smaller pores when compared with SIMs and as can be seen in Figure 1D, despite the use of much higher magnification ratio, the pores are not visualized. This is an advantageous aspect, enhancing the contact area between air and sorption surface in comparison with SIMs. However, smaller pore size could possibly bring a difficulty in removing the adsorbed moisture when recharging the Zeolite 13X. This could lead to higher regeneration temperatures,  $T_{reg}$ , which is an undesired situation in sorption heat storage processes.

The Gen2 testing rig (see: Figure 2-A) used in the previous research had a flat absorbent bed where the SIM material was placed on a perforated tray and air flow was perpendicular to the perforated surface. In this system there was no additional configuration allowed for to improve diffusivity and mass transfer, as the primary aim of the testing rig was to carry out a comparative performance analysis of a large number of SIM's over a short period of time. Numerical

modelling simulations on Ansys Software of the Gen2 rig showed that high resistance occurs at the reaction front which both increases the pressure drop across the absorbent bed and reduces the diffusivity and thus moisture transfer, particularly when there is an increase in SIM layer depth. This served to limit scaling-up the THS system using the Gen2 rig design.

A new testing rig (*i.e.* Gen 3), was designed and developed to demonstrate the concept/design 261 for large scale THS applications. This system (see: Figure 2-B) was designed to investigate the 262 hygrodynamic and thermodynamic performance of the system when using perforated tubes to 263 facilitate vapour diffusion to the SIM to reduce the effect of the reaction front. Compared to the 264 Gen2 rig, the Gen3 reaction chamber (8) is rectangular shaped (500 mm x 250 mm x 200 mm) 265 with a sloping roof to facilitate post absorbent airflow and is constructed of aluminium with 266 welded seams. Ten perforated tubes, d = 20mm, made up of 0.55 mm thick perforated 267 268 aluminium sheet were placed vertically inside the reactor in two parallel rows with a horizontal distance, d = 100 mm between each (x and z direction). The tubes are connected to an external 269 manifold (12) to equalise airflow to each tube, with the top end of the tubes sealed in order to 270 achieve sufficient internal pressure, providing air flow laterally to the absorbent (9). Use of 271 perforated tubes embedded inside the sorbent enhances to contact area of air and sorbent, 272 273 provides uniform vapour diffusion and heat/mass transfer. In a flatbed reactor (Gen2), the vapour uptake at the reaction front is higher than the rest of the sorbent in the bed. The reaction 274 front wets in a short period of time, blocking air flow, reducing heat output and increasing 275 276 pressure drop. To overcome these issues, the Gen3 reactor was proposed as an improved design to enhance the thermal performance of THS process. 277





Figure 2 – Schematic diagram of (A) the Gen2 and (B) the Gen3 experimental test rigs.

Humidification of the inlet air is provided using an evaporative pad matrix placed inside a 280 281 rectangular shaped wick chamber (11). Air flow through the wick chamber is parallel to the evaporative pads, enabling moisture enhancement of the inlet air before entering the reaction 282 chamber. An Xpleair (UK) XID series, inline duct fan (1) (d = 150 mm) is used to provide air 283 flow and is connected to ducting (d = 100 mm) via a reducer. To eliminate thermal losses to the 284 external environment, the complete system is insulated using 25 mm thick, foil lined glass wool. 285 286 Temperature and relative humidity (RH) were recorded using the EK-H4 Eval Kit for Temperature - Humidity Sensors from Sensiron, AG, Switzerland. Three sensor locations were 287 used -(2) ambient, (3) manifold inlet and (4) reactor outlet. 288



289 290

Figure 3 – Graphical flow chart of the experimental methodology.

291 The experimental methodology was divided into two phases (see: Figure 3). The first phase included a comparative energetic, exergetic and hygrothermal analysis of the three selected 292 materials' performance in the Gen2 and newly developed Gen3 rigs. In the second phase, the 293 best performing material from the first phase would be selected for parametric analysis using 294 the Gen3 rig. This analysis would chart the effect on performance (i.e. temperature lift and 295 moisture uptake) of i) tube hole diameter and ii) air flow rate. Additionally, both the long and 296 297 short term cyclic behaviour of the SIM material with correlations between mass change,  $\Delta w$ and temperature change,  $\Delta T$  were investigated. 298

## 300 **3.** Comparison of performance between Gen2 and Gen3

In this section an analysis of both the energetic and exergetic experimental results collected 301 302 during the testing period is presented and discussed with the formulas used in the analysis given in Table 1a-c. All samples were prepared by oven drying at  $T \approx 150$  °C for a period, t > 24 h to 303 achieve the condition  $m_{dry} = 0$  kg/kg. The dry SIM was then placed in a mesh tray and allowed 304 to cool in a desiccator for t = 2 h prior to testing. When cooled, the material was placed into 305 the reaction chamber and the rig sealed. During the charging of the materials, partial vapour 306 pressures  $(P_v)$  for SIM-3a and SIM-3f were varied in the range of 764  $\rightarrow 0$  mbar and 853 $\rightarrow 0$ 307 mbar indicating that both SIMs were fully regenerated at 150 °C. On the other hand,  $P_{\nu}$  for 308 Zeolite 13X dropped from 582 to 82 mbar and then remained constant demonstrating that 309 Zeolite 13X requires higher temperatures for fully desorption to occur. As the aim was to test 310 material performance under identical operating conditions, no further desorption at higher 311 temperatures were applied to Zeolite 13X. As a result, its performance sharply dropped over 312 313 repeating discharging cycles, whereas performance of the SIM's were much steadier as discussed in detail in the following sections of the paper. 314

For the discharging cycle (absorption), the humidifier was connected and the psychrometric state of the airflow monitored. When the desired humidity level was reached, the inlet valve was opened. Each test was carried out over two short discharging cycles of duration  $t_{cycle} = 180$ min each with charging of the material occurring between each cycle. For the charging cycle (desorption) the humidifier was disconnected and the heating unit activated and set to the desired regeneration temperature (T = 90 °C). The charging cycle was deemed to be complete when;

322  $RH_{out} = RH_{in}$  or  $\Delta m \le 2\%$  or  $T_{in} = T_{out}$ 

			Equation
Definition	Unit	Equation	No.
Instantaneous heat gain	kW	$\dot{Q}_g = \dot{H}_{out,dr} - \dot{H}_{in,dr}$	1a
		$\dot{Q}_g = \dot{m}_{dr}.c_p.\left(T_{out,dr} - T_{in,dr}\right)$	1b
Energy density	Wh/g	$E_d = \frac{E_{cum,dr}}{\Delta m_{ads}}$	2
	kWh/m <sup>3</sup>	$E_{d,dr} = \frac{E_{cum,dr}}{V_{ads}}$	3
Mass increase	g	$\Delta m_{dr} = M_{wv} = M_w - M_d$	4
Mass uptake ratio		$f_{dr} = \frac{M_{ads,x} - M_{ads,d}}{M_{ads,d}}$	5
Absolute humidity	g/kg	$w = 216.7. \left[ \frac{\frac{RH}{100\%} \cdot 6.112. \exp\left(\frac{17.62.T}{243.12 + T}\right)}{273.15 + T} \right]$	6
Cumulative thermal energy generation	kWh	$E_{cum} = \dot{m}_{dr}.c_p.\int_{0}^{t_d} (T_{out,dr} - T_{in,dr})dt$	6
Exergy gain	kW	$\vec{Ex}_g = (\vec{Ex}_{out,dr} - \vec{Ex}_{in,dr})$	7a
		$\dot{Ex}_{g} = \dot{m}_{dr} \cdot \left[ \left( h_{out,dr} - h_{in,dr} \right) - T_{a} \cdot \left( s_{out,dr} - s_{in,dr} \right) \right]$	7b
		$\dot{Ex}_g = \dot{m}_{dr}.c_p.\left[\left(T_{out,dr} - T_{in,dr}\right)\right]$	7.
		$-T_a \cdot \ln\left(\frac{T_{out,dr}}{T_{in,dr}}\right)$ ]	/c
СОР		$COP_{dr} = \frac{\dot{Q}_{g,avg}}{\dot{W}_f}$	8

Table 1a- Equations for analysis of the discharging process

			Equation
	Unit	Equation	No.
Instantaneous heat	kW	$\dot{Q}_{tr} = \dot{H}_{in,cr} - \dot{H}_{out,cr}$	9a
transfer to absorbent		$\dot{Q}_{tr} = \dot{m}_{cr}.c_p.\left(T_{in,cr} - T_{out,cr}\right)$	9b

Cumulative energy  
transfer to absorbentkWh
$$E_{cum,c} = \dot{m}_{cr} \cdot c_p \cdot \int_{0}^{t_c} (T_{in,cr} - T_{out,cr}) dt$$
10Desorption heat transferWh/g $E_{d,cr} = \frac{E_{cum,cr}}{\Delta m}$ 11Removed moistureg $\Delta m_{cr} = M_{wv} = M_w - M_d$ 12Mass release ratio--- $f_{cr} = \frac{M_{ads,w} - M_{ads,x}}{M_{ads,w}}$ 13 $Ext_{tr} = (Ex_{in,cr} - Ex_{out,cr})$ 14akW $Ex_{tr} = \dot{m}_{cr} \cdot [(h_{in,cr} - h_{out,cr}))$ 14babsorbent $Ex_{tr} = \dot{m}_{cr} \cdot c_p \cdot [(T_{in,cr} - T_{out,cr}))$ 14cCharging efficiency% $\eta_{cr} = \frac{\dot{Q}_{tr}}{W_f + \dot{Q}_h}$ 15

325 Table 1b - Equations for analysis of the charging process

326

			Equation
Definition	Unit	Equation	No.
1 <sup>st</sup> law efficiency		$\eta_{I,rxn} = \frac{\dot{Q}_{g,ave}}{\dot{Q}_{tr,ave}}$	16
2 <sup>nd</sup> law efficiency		$\eta_{II,rxn} = \frac{\vec{E}x_{g,ave}}{\vec{E}x_{tr,ave}}$	17

327 Table 1c - Equations for analysis of system efficiencies

328 The  $P_v$  of the outlet air during the charging cycles of SIM-3a, SIM-3f and Zeolite 13X were in

the range of  $375 \rightarrow 21$  and  $416 \rightarrow 14$  and  $310 \rightarrow 63$  mbar respectively. Some residual moisture

remained in all materials at  $T_{reg} = 90$  °C (the moisture content was highest in Zeolite 13X and

331 lowest in SIM-3f after desorption).

In Figure 4, the discharging inlet and outlet temperatures,  $T_{in}$  and  $T_{out}$ , of SIM 3a, SIM-3f and 332 Zeolite 13X tested in both the Gen2 and Gen3 rigs are presented with the full data set from test 333 and subsequent analysis summarized in Table 2. The purpose of these tests was to compare the 334 335 Gen2 and Gen3 testing rigs and demonstrate any performance improvement. In THS systems, contrarily to both SHS and LHS systems, effective mass transfer (moisture) is required, which 336 can significantly reduce performance as the size of the THS system increases. If we assume that 337 the heat storage capacity of all these systems is directly proportional to the amount of material 338 employed, then novel designs which provide efficient moisture diffusion are therefore required 339 to enable efficient sorption processes in larger storage units. 340

An 'open' THS system operation is based on the temperature lift of a building's air due to the energy conversion associated with moisture absorption. Due to the thermochemical reaction, there is a sharp temperature lift of output air at the beginning of the reaction and, as time passes, the moisture content inside the reactor increases and moisture sorption rate of THS material (*i.e.* sorption kinetics) slows down causing a drop in temperature. For thermal analysis of the tests, four measures are used here:

- 3471. Maximum output temperature,  $T_{out, max}$ , which is the peak temperature reached in each348single cycle
- 349 2. End state temperature lift,  $\Delta T_{180}$ , which represents the temperature lift at the end of the 350 cycle *i.e.*  $T_{out} - T_{in}$  @ t = 180 min
- 351 3. Dynamic output temperature drop, c, which is the gradient from  $T_{out, max}$ , to  $T_{out, 180}$ , 352 (dT/dt)
- 4. Average temperature lift,  $\Delta T_{avg}$ , which is the average temperature differential over the full cycle i.e.  $T_{out} - T_{in} / 180$

The results show that the performance of all three materials increased across all four measures when using the Gen3 testing rig as opposed to the Gen2 rig.





Figure 4 – Three hour limited generation cycles for SIM-3a, SIM-3f and Zeolite 13X using the Gen2 and Gen3 experimental rigs.

To ease notation in the text, the first cycle of each test is denoted as <sup>(1)</sup> whilst the second cycle 360 is noted as <sup>(2)</sup>. The results for SIM-3a (Vermiculite/CaCl<sub>2</sub>) clearly indicate the significant 361 improvement in Gen3 rig with an average temperature lift  $\Delta T_{avg} = 23 \ ^{\circ}C^{(1)}$  and 19.9  $^{\circ}C^{(2)}$ 362 compared with 12.8  $^{\circ}C^{(1)}$  and 10.7  $^{\circ}C^{(2)}$  in Gen2. In both cycles of the Gen2 rig, a sharp drop in 363 outlet temperature,  $T_{out}$  was observed with dynamic output temperature drops of,  $c = 0.092^{(1)}$ 364 and 0.067<sup>(2)</sup> for the Gen2 rig compared with 0.061<sup>(1)</sup> and 0.055<sup>(2)</sup> for Gen3 which are shallower 365 and indicate better performance due to the increased diffusion and steadier vapour absorption 366 of SIM-3a in Gen3 after the wetting of the reaction front. Initial maximum temperatures are 367

also higher in Gen3 with,  $T_{out, max} = 50 \text{ °C}^{(1)}$  and 45 °C<sup>(2)</sup> as opposed to 45 °C<sup>(1)</sup> and 40 °C<sup>(2)</sup>. Although there was only a 5 °C difference observed in  $T_{out, max}$  it is the end state temperature difference that indicates the superior performance of Gen3 over Gen2 with  $\Delta T_{180}$  values of 19.9 °C<sup>(1)</sup> and 16.5 °C<sup>(2)</sup> in Gen3 against 7.8 °C<sup>(1)</sup> and 7.1 °C<sup>(2)</sup> in Gen2.

For SIM-3f (Vermiculite/CaCl<sub>2</sub>/LiNO<sub>3</sub>) both the average and peak temperature lift was higher in Gen 3. Although the temperature lifting of SIM-3f was poor in Gen2, it showed a steadier performance across both cycles with gradients  $c = 0.025^{(1)} - 0.020^{(2)}$  in Gen2 and  $0.065^{(1)} - 0.038^{(2)}$  in Gen3. End state temperature difference,  $\Delta T_{180}$  for cycle 1 was similar in Gen2 and Gen3, however, in cycle two, Gen3 was considerably higher,  $\Delta T_{180} = 16.2$  °C than 13.7 °C in Gen2. Average temperature lift was also higher for Gen 3,  $\Delta T_{avg} = 14.3$ °C<sup>(1)</sup> and 18.5°C<sup>(2)</sup> as opposed to Gen 2 with  $\Delta T_{avg} = 10.2$  °C<sup>(1)</sup> and 12.4 °C<sup>(2)</sup> indicating improved performance.

Zeolite 13X's performance was also significantly enhanced using the perforated tubes (Gen3) 379 in comparison to Gen2. A sharp drop was observed in both cycles for the Gen 2 rig with  $\Delta T_{180}$ 380 = 9.5 °C<sup>(1)</sup> and 3.6 °C<sup>(2)</sup> representing a falloff in performance of 5.9 °C between the cycles. In 381 Gen 3 however, performance is much steadier with  $\Delta T_{180} = 17.7 \ ^{\circ}C^{(1)}$  and  $16.1 \ ^{\circ}C^{(2)}$  representing 382 383 a small drop of 1.6 °C between cycles. The improved performance in Gen 3 was due to the uniform air flow and better diffusivity through the material. This condition is evidenced with 384 the comparison of the  $\Delta RH_{avg}$  (see: Table 2) achieved in Gen 2 and Gen 3 and demonstrates 385 three facts; 386

3871.Reducing  $\Delta RH_{avg}$  (32.5 %<sup>(1)</sup>  $\rightarrow$  24.4 %<sup>(2)</sup>) between cycles led to a notable performance388drop of Zeolite 13X ( $\Delta T_{ave} 20 \,^{\circ}C^{(1)} \rightarrow 12.5 \,^{\circ}C^{(2)}$ ) in the Gen2 testing rig. This was an389expected outcome, as the change in  $P_v$  across the material is directly related with390sorption heat generation. However, despite the targeted drop (per 1% change) in  $\Delta RH_{avg}$ 391being < 0.5 °C, experimental results showed that the drop is ~1 °C.</td>

392 2. Steady  $\Delta RH_{avg}$  (75.3%<sup>(1)</sup>  $\rightarrow$  75.7%<sup>(2)</sup>) provided a more stable performance without any 393 significant drop in the Gen3 testing rig. 394 3. The higher  $\Delta RH_{avg}$  in Gen3 enabled higher average temperatures,  $\Delta T_{avg} = 5.2 \,^{\circ}C^{(1)}$  and 395 9.5  $^{\circ}C^{(2)}$  with consequently higher energy density,  $E_d$  of 13.8<sup>(1)</sup> and 35.2<sup>(2)</sup> kWh/m<sup>3</sup>.

The cyclic energetic ( $\eta_I$ ) and exergetic ( $\eta_{II}$ ) efficiencies of the materials in Gen2 and Gen3 are presented in Figure 5. SIM-3a provided improved  $\eta_I$  and  $\eta_{II}$  in the Gen3 rig in both cycles.  $\eta_I^{(1)}$ for SIM-3a varied between 0.79 $\rightarrow$ 0.71 whereas  $\eta_I^{(2)}$  was found to be 0.63 $\rightarrow$ 0.53. As a result of the exergy losses and exergy destruction,  $\eta_{II}$  was much lower for both test rigs.  $\eta_{II}^{(1)}$  was calculated as 0.25 $\rightarrow$ 0.19 whilst  $\eta_{II}^{(2)}$  was 0.18 $\rightarrow$ 0.13 in two repeating cycles.  $\eta_I$  for Sim-3f was similar in both test rigs. Using Gen3,  $\eta_I$  varied between 0.52- 0.61 for both test rigs,  $\eta_{II}^{(1)}$  was 0.04 and  $\eta_{II}^{(2)}$  was 0.09-0.013 in two cycle testing of SIM-3f.

403





Figure 5 – Energetic and exergetic efficiency of materials in Gen2 and Gen3 testing rigs

Although the performance of Zeolite 13X in the Gen2 rig was superior, it dropped sharply in the following cycle due to the poor moisture desorption (*i.e.* regeneration).  $\eta_I^{(1)}$  for the initial cycle of Zeolite 13X was 0.75 which was the highest among all performed tests.  $\eta_I^{(1)}$  was found

to be only 0.48 in the repeating cycles however, which was the lowest obtained efficiency. The Zeolite 13X's performance in the Gen3 rig was found much steadier, where  $\eta_I^{(2)}$  was 0.58 $\rightarrow$ 0.53. In terms of second law performance,  $\eta_{II}^{(1)}$  dropped substantially to the range of 0.21 $\rightarrow$ 0.05, whereas  $\eta_{II}^{(2)}$  was relatively steadier (0.16 $\rightarrow$ 0.11). Results indicate that SIM-3a performs best in terms of both energetic-exergetic efficiencies and also has the most promising thermal stability.

416 Mass uptake ratio,  $f_{dr}$ , for the discharging cycle and mass loss ratio,  $f_{cr}$ , for the charging cycle 417 of all materials in Gen2 and Gen3 rigs are presented in Figure 6. According to previous testing 418 results, the moisture removal ratio (MRR= $m_{ads,dr}/m_{des,cr}$ ) in Gen2 rig was 0.91, 0.95 and 0.72 419 for SIM-3a, SIM-3f and Zeolite 13X respectively. For the Gen3 rig, MRR was found to be 0.95, 420 0.93 and 0.77 for the same order of materials. A low MRR indicates a drop in desorbed moisture 421 during the charging cycle which results in a drop of adsorption energy and thus poor heat output 422 in following discharging cycles.

This suggests that, SIM-3a and SIM-3f effectively regenerate at the applied regeneration temperature ( $T_{reg} = 90$  °C) with an MRR > 0.9. The MRR for Zeolite 13X was < 0.8 however, explaining the reason for its poor cyclic ability and thermal stability under the same operating conditions. Theoretically, assuming a constant inlet air  $P_{\nu}$  for all materials, the corresponding  $T_{out}$  values will be in the range of  $T_{out,SIM-3a} > T_{out,SIM-3f} > T_{out,Zeolite}$  due to the higher MRR and higher heat output per unit of moisture uptake of SIM's.

- 429
- 430





Figure 6 – Mass uptake ratio of the materials in Gen2 and Gen3 testing rigs

- 433 Two other important measures for comparing material performance in both testing rigs are  $E_d$ 434 435 and  $COP_{dr}$  as presented in Figure 7. The  $E_d$  used in the analyses is the ratio of total heat output (total enthalpy change of air across the sorbent) per m<sup>3</sup> of the sorption material over the 436 discharging period under a constant inlet air  $P_v$  of 20 mbar.  $COP_{dr}$  is the ratio of heat output to 437 total electrical work input to the system during discharging. Improved  $E_d$  was obtained for SIM-438 3a and Zeolite 13X in Gen3 rig, whilst  $E_d$  SIM-3f was slightly higher using the Gen2 rig. Using 439 the Gen3 rig, the  $E_d^{(1)}$  and  $E_d^{(2)}$  of SIM-3a was between 104 $\rightarrow$ 80 kWh/m<sup>3</sup> and 112 $\rightarrow$ 97 kWh/m<sup>3</sup> 440 respectively. SIM-3f provided an  $E_d$  of 101 kWh/m3 in the 2<sup>nd</sup> cycle of testing in Gen2 rig, 441 which was the second highest among all performed cycles. In contrast, the lowest  $E_d$  achieved 442 was in the second cycle testing of Zeolite 13X in the Gen2 rig, due to the poor heat output in 443 that discharging cycle. The summary of the obtained  $E_d$ 's across all tests are presented in Table 444 2. 445
- Zeolite 13X provided the highest  $COP_{dr}$  in the Gen2 rig, which was approximately 21, however a substantial drop was observed in the second cycle, similar to the other measures as presented

448 previously. When the  $COP_{dr}$  average across two cycle testing of materials was considered, 449  $COP_{dr}^{(1)}$  was 12, 12, 17 for SIM-3a SIM-3f and Zeolite 13X respectively. For the same order, 450  $COP_{dr,ave}^{(2)}$  was calculated as<sup>3</sup> 17, 13 and 15. Whilst the  $COP_{dr,ave}^{(1)}$  of both Zeolite 13X and 451 SIM-3a were found to be equal, the steadier performance of SIM-3a over further repeating 452 cycles would probably lead to higher COP values.



Figure 7 – Energy density and COP of the materials in Gen2 and Gen3 testing rigs Looking holistically across all the chosen performance criteria ( $Q_g$ ,  $Ex_g$ ,  $\Delta T$ , MRR,  $\eta_I$ ,  $\eta_{II}$ ,  $COP_{dr}$ and  $E_d$ ), the most promising results were for SIM-3a in the Gen3 rig. CaCl<sub>2</sub> is highly hygroscopic and will continue to absorb moisture until deliquescence occurs. The combination of this remarkable property with its high  $E_d$  (45 kJ/mole) makes it a very promising candidate for domestic THS applications.

Whilst it was expected that SIM-3f would perform better than SIM-3a however this couldn't be achieved in the experiments. This could be due to the change in chemical structure of  $LiNO_3$ and  $CaCl_2$  when mixed, thereby altering the thermochemical properties of both salts.  $CaCl_2$ shows a rapid response to moisture and has a high sorption rate when used individually.

Conversely, LiNO<sub>3</sub> has a slow response to moisture and low sorption rate resulting in a lower 465 but steadier heat output. As the water attraction of CaCl<sub>2</sub> is higher, it has a higher water 466 desorption temperature than LiNO<sub>3</sub> which is not desired. The salts were mixed to create a 467 468 composite with the aim of lowering the desorption temperature and increasing the moisture sorption-desorption stability of  $CaCl_2$  and, as a result, consuming less energy in charging cycles. 469 However, LiNO<sub>3</sub> dominated the new composite and the sorption rate remained low. 470 471 Furthermore there wasn't any major increase in desorption rate of SIM-3f when compared with SIM-3a indicating that the drop of regeneration temperature was not significant. All these 472 outcomes showed that the individual use of CaCl<sub>2</sub> is more advantageous. 473

SIM-3a has a lower critical humidity thereby higher affinity to water vapour when compared with SIM-3f and Zeolite 13X. The uniform allocation of salt and larger pore size of SIM-3a (See: Figure 1) promotes better vapour sorption and desorption in charging and discharging cycles. Additionally, as the salt is located between the lamellas rather than randomly sticking on the vermiculite surface, redistribution of salt / pore blocking are minimised over repeating cycles. These aspects explain the better hygrothermal and cyclic performance of SIM-3a among the three tested absorbents.

Utilising CaCl<sub>2</sub> as the thermochemical media and vermiculite as the host matrix constitutes a
 spectacular composite absorption material for conversion and storage of solar energy or waste
 heat.

	Test	Cycle	∆RH	(%)	$\Delta T$	(°C)	f	Ecum	Excum	Q (	<b>W</b> )	Ex	(W)	$E_d$	
	rig	No	Peak	Avg.	Peak	Avg.	$(\mathbf{g}_{wv}/\mathbf{g}_{abs})$	(Wh)	(Wh)	Peak	Avg.	Peak	Avg.	kWh/m <sup>3</sup>	Wh/g
SIM-3a	Gen 2	1	47.9	27.6	24.6	12.8	0.24	209	3.4	133.3	69.5	4.7	1.1	104.5	1.61
		2	47.3	27.6	22.7	10.7	0.22	161	2.1	120.2	58.3	3.1	0.7	80.5	1.40
	Gen 3	1	76.1	66.7	28.6	23.0	0.47	1123	35.1	464.1	373.1	17.6	11.6	112.3	0.67
		2	83.5	71.7	25.3	19.9	0.46	971	24.8	410	323.6	14.2	8.2	97.1	0.59
SIM-3f	Gen 2	1	39.2	29.5	13.3	10.2	0.22	166	0.6	71	55	0.7	0.2	83.3	1.26
		2	30.8	23.9	14.3	12.4	0.21	202	0.8	77	65	0.7	0.2	101	1.64
	Gen 3	1	65.2	50.3	23.0	14.3	0.32	697	10.3	374.8	231.8	11.5	3.4	69.7	0.77
		2	65.9	61.2	21.7	18.5	0.36	901	19.1	352.6	300.5	8.7	6.3	90.1	0.66
Zeolite 13X	Gen 2	1	52.9	32.5	29.2	20	0.22	162	4.0	157.6	108.2	5.5	2.6	81.0	0.65
		2	46.2	24.4	23.4	12.5	0.18	101	1.1	124.7	67.8	2.5	0.7	50.5	0.49
	Gen 3	1	94.8	75.3	33.4	25.2	0.18	948	25.8	435.9	327	17.6	8.5	94.8	0.69
		2	90.3	75.7	30.3	22.0	0.17	857	17.5	393.5	285	11.3	5.8	85.7	0.65

484 Table 2 - Full results data set for the Gen2 & Gen3 testing rigs material based performance comparison.

#### 485 **4. Parametric analysis of operating conditions**

In this section the experimental results of the best performing absorbent (SIM-3a), tested in the Gen3 rig using different tube configurations and different mass flow rates are presented. The aim was to investigate the effect of the perforated tube's hole diameter (acting as an air diffuser) on heat and mass transfer. The thermal performance of SIM-3a using three different mass flow rates was also analysed to determine the optimum operational conditions.

# 491 **4.1. Vapour Diffusion - tube configuration**

In 'open' THS reactor design, perforated diffuser tubes can be considered crucial components 492 and their effectiveness can determine the performance of the entire heat storage process. As in 493 494 the previous section, the measures  $\Delta T_{180}$ ,  $\Delta T_{avg}$  and  $T_{out, max}$  are used to determine the heat storage effectiveness. In THS process, the aim is to achieve a steady temperature output (see: 495 Figure 4) rather than a very high peak at the beginning followed by a sharp drop. Considering 496 that building heat loads are dynamic, heat storage performance should be predictable to allow 497 simple design and management for space heating applications. In this context perforated tubes 498 499 with 1 mm  $(d_1)$ , 2 mm  $(d_2)$  and 3 mm  $(d_3)$  hole diameters were tested to compare their performance and determine the most suitable size. The diameter of the holes in the air diffusers 500 can significantly influence the thermal performance of the THS system as hole size has an 501 502 impact of the pressure and velocity of the air diffusing into the sorption material. To investigate the impact of hole size on THS performance, three different perforated tubes were tested. The 503 temperature and RH variation of the process air during testing is given in Figure 8 and Figure 504 9. It is clearly seen from Fig. 4 that  $d_3$  provided a sharp temperature lift ( $T_{out, max} > 48$  °C) at the 505 beginning of the reaction followed by  $d_1$  and  $d_2$  with  $T_{out, max} > 42$  °C. In terms of overall 506 507 performance,  $\Delta T_{avg}$  was found to be very similar for all three hole sizes (16.1 °C, 16.4 °C and 15.9 °C for d<sub>1</sub>, d<sub>2</sub> and d<sub>3</sub> respectively). 508



509
510 Figure 8 – Temperature variation of SIM-3a with different tube configurations in the Gen3
511 testing rig.



Figure 9 – Relative humidity variation of SIM-3a with different tube configurations in the Gen3
 testing rig.

The cumulative energy and exergy measures,  $E_{cum}$  and  $E_{xcum}$  confirm the greater performance of  $d_2$  with values of 640 Wh and 12.3 Wh compared with  $d_1$  and  $d_3$  (630 Wh/618 Wh and 9.6 Wh/10.2 Wh respectively).

Figure 9 illustrates the RH of both inlet and outlet air for cycles with different tube 520 configurations. As the novel evaporative humidification unit consists of evaporative pads 521 without any additional moisture supply (e.g. water spray, atomizer, ultrasonic humidifier), a 522 controlled amount of vapour was added to the air in each test, however there was still a slight 523 variation to reactor inlet RH due to the varying humidity of the laboratory environment during 524 each testing period. The higher  $T_{out, max}$  observed for  $d_3$  could be due to the slightly higher inlet 525 RH where  $d_3$  reached RH = 85% whereas  $d_1$  and  $d_2$  were lower at RH  $\approx$  77% at the end of 180 526 minutes. The moisture uptake ratio, f was found as 0.28, 0.29 and 0.31  $g_{wv/}g_{abs}$  for  $d_3$ ,  $d_1$  and  $d_2$ 527 respectively. Whilst there is not any significant difference between the effectiveness of 528 perforated tubes with different hole sizes,  $d_2$  seems to be the best candidate for achieving a 529 steadier performance over longer periods of heat storage. Therefore  $d_2$  was selected for the 530 remaining tests investigating the effect of mass flow rate on thermal performance, evaluating 531 the cyclic stability and long term behaviour of SIM 3a. 532

### 533 **4.2.** Air mass flow rate

Although 'open' THS is a relatively simple method for heat storage, it involves a complex process of energy conversion via absorption where mass (moisture transfer from air to the adsorbent) and heat (from adsorbent to the process air) transfer is dynamic and occurs simultaneously. The mass flow rate of the inlet air has therefore a significant effect on overall heat storage performance. This includes the influence of both moisture and air which are either directly or indirectly related with achievable temperature lift,  $\Delta T$ .

540 For instance, a high mass flow rate can provide higher heat generation as it carries more 541 moisture to the absorbent however a higher amount of dry air is thus also required to be heated

at the same time. Simply, increasing humidity has a positive influence on  $\Delta T$  while increasing 542 the dry air volume has a negative influence. A high rate of moisture absorption (from higher 543 RH) also creates a "wetting effect" on the absorbent which can cause sensible cooling of both 544 545 the absorbent and the process air. It should also be noted that the heat storage capacity of any finite mass of sorption material is limited and a high rate of moisture sorption will lead to high 546 initial thermal power release from the absorbent, but with low process time as the temperature 547 lift drops sharply in a short period of time. Conversely, a low mass flow rate may lead to 548 insufficient moisture supply to the absorbent and may not provide enough pressure for uniform 549 air and moisture diffusion throughout the entire absorbent. This condition can lead to several 550 undesired consequences such as low temperature lift, low reaction kinetics, non-uniform 551 moisture sorption and moisture condensation at the reaction front. To investigate the effect of 552 air mass flow rate on discharging output temperature, a one cycle test under three different air 553 mass flow rates was performed. 554

Figure 10 illustrates the inlet and outlet air temperature for three different cycles with three air mass flow rates (0.012 kg/s, 0.015 kg/s and 0.02 kg/s). The results demonstrate considerably improved performance with the mid-range flow rate (0.015 kg/s) with  $T_{out, max} = 50$  °C and  $\Delta T_{180}$ = 20 °C compared to the lower (0.012 kg/s) and higher (0.02 kg/s) flow rates.

The output temperature from the reactor is a function of the air mass flow rate and vapour 559 absorption rate of the sorbent. With an increasing air mass flow rate, the amount of air to be 560 heated per unit time is greater. Therefore, a higher mass flow rate (0.02 kg/s) leads to a drop in 561  $T_{out}$ . On the other hand, a low air mass flow rate (0.01 kg/s) reduces the amount of vapour 562 supplied to the sorbent. As a result, any absorption heat generated remains insufficient to 563 increase the air temperature above 45 °C. As seen in Figure 10, when a lower amount of vapour 564 supply is used, the rate of heat generation is lower; therefore,  $T_{out}$  is much steadier at a low air 565 566 mass flow rate (0.01 kg/s) compared with the higher mass flow rate. At a mid-range air mass flow rate (0.015 kg/s) ratio of the amount of air to be heated and vapour supplied to the sorbent 567

per unit time is optimal. This condition led to a substantial increase in  $T_{out}$  when compared with



569 both the higher and lower air mass flow rates.

Figure 10 - Temperature variation of SIM-3a with different air mass flow rates in the Gen3
testing rig.

These results demonstrate that whilst there is not any direct correlation between THS performance and air flow rate / humidity, each reactor design will have a unique optimum flow rate which should be carefully analysed (numerically or experimentally) in order to achieve the optimum thermal output from the system.

# 578 5. Cyclic analysis of material performance

579 **5.1.** Analysis of a single long cycle

580 The long term performance of one cycle of SIM-3a, which provided the most promising results

previously are presented in Figure 11. To investigate the maximum thermal energy that can be

extracted from SIM-3a using the Gen3 testing rig, this cycle was allowed to run until the

583 condition  $T_{out} = T_{in} + 3$  °C was achieved (at the end of 20 hours for this case).



584 585

Figure 11 – Thermal performance of SIM-3a over 1200 min. testing in Gen3 testing rig

586 During the test period the total thermal energy output reached 2.93 kWh in comparison with 587 the 1.12 kWh at the end of first three hours in the previous tests (see: Table 2) with mass uptake 588 tripling to 1.41 from 0.47  $g_{wv}/g_{abs}$ . It is interesting that 2.93 kWh was achieved using only 0.01 589 m<sup>3</sup> of storage volume, suggesting that THS has remarkable potential for reducing the space 590 requirement for heat storage systems in future low/zero carbon buildings.

591 Figure 12 illustrates the correlation of  $\Delta w$  and  $\Delta T$  over 20 hours testing of SIM 3a where  $\Delta w$  is the absolute humidity difference ( $w_{in}$ -  $w_{out}$ ) and  $\Delta T$  is the temperature difference ( $T_{out}$ -  $T_{in}$ ) of 592 inlet and outlet air during the discharging cycle. During the test period (t = 20 h), it can be 593 observed that the correlation between  $\Delta w$  and  $\Delta T$  is almost linear and independent of time. In 594 theory, this would allow monitoring of performance drops as a result of reducing mass uptake 595 trends over repeated cycles. For instance, the rate of mass uptake would decrease with the 596 reduced inlet air partial pressure, air mass flow rate or reduced bed height in the discharging 597 cycle. As a result, the temperature lift,  $\Delta T$ , will be lower. Utilizing the correlation presented in 598 599 Figure 12, would allow determining the best possible  $\Delta T$  for any particular operational

600 condition or reactor configuration. Recognizing and using this correlation in the future should

allow easier and more efficient design and management conditions for THS systems.



602 603

Figure 12 – Correlation between  $\Delta w$  and  $\Delta T$  for SIM-3a in the Gen3 rig

# 604 5.2. Analysis of multiple short cycles

The last stage of testing was to analyse the cyclic behaviour of SIM-3a in order to simulate its 605 performance for long term (cyclic) heat storage applications. Based on the previous results, an 606 air flow rate of 0.015 m<sup>3</sup>/s and perforated tubes with hole diameter of d = 2 mm were used 607 during the tests. Due to technical difficulties with the rig during these cycles, SIM-3a was 608 recharged at T = 90 °C for 24 hours following each discharging cycle in an externally located 609 oven. For that purpose, all material was removed from the reactor and placed inside the oven in 610 611 a perforated tray. As a natural convection oven was used for desorbing the moisture, charging duration was long (close to 24 hours). If charging was done in the reactor, it would be expected 612 to be shorter due to the forced convection applied with the air flow. This would enhance the 613 614 desorption rate thereby using charging heat input more efficiently.

Figure 13 represents the inlet and outlet temperatures and thermal energy output in each of the four cycles.  $\Delta T_{180}$  showed a decreasing trend from the 1<sup>st</sup> cycle to 4<sup>th</sup> cycle in the order of 19.5 °C  $\rightarrow$  17.2 °C  $\rightarrow$  14.8 °C  $\rightarrow$  13.2 °C which was somewhat expected. Similarly, cumulative energy outputs,  $E_{cum}$ , were 1.12 kWh  $\rightarrow$  0.96 kWh  $\rightarrow$  0.87 kWh  $\rightarrow$  0.74 kWh with cumulative exergy outputs,  $E_{xcum}$ , calculated as 0.035 kWh  $\rightarrow$  0.024 kWh  $\rightarrow$  0.018 kWh  $\rightarrow$  0.013 kWh in the order 1<sup>st</sup>  $\rightarrow$  4<sup>th</sup> cycle respectively.



621 622

Figure 13 – Cyclic performance of SIM-3a in the Gen3 testing rig

In terms of energy output this corresponds to a performance drop of 14% for the  $1^{st} \rightarrow 2^{nd}$  cycle, 623 9% for the  $2^{nd} \rightarrow 3^{rd}$  cycle and 14% for the  $3^{rd} \rightarrow 4^{th}$  cycle. One possible reason for the 624 performance drop could be insufficient drying of the material as an electrical oven was used for 625 recharging the material (*i.e.* static air). Usage of a hot/dry air flow through the material could 626 be more effective as air convection could significantly contribute to moisture removal from the 627 material. Greater drying of the absorbent would undoubtedly achieve greater cyclic 628 performance of SIM-3a as the material did not show any physical degradation over the cyclic 629 testing. The performance drop is the result of the reducing trend of mass uptake over the four 630

repeated cycles supporting the correlation discussed earlier between moisture supplied to the material and temperature lift (See: Figure 12). This is due to the residual moisture remaining in the material at the applied  $T_{reg}$  (90 °C). If  $T_{reg}$  were increased to 120 °C, theoretically anhydrous SIM-3a would be achieved and at that condition, steady  $T_{out}$  profiles could be obtained over repeating cycles. However it should be noted that, increasing  $T_{reg}$  will significantly increase the required sorption heat and this could lead to a sharp drop in THS cyclic efficiency. Therefore,  $T_{reg} = 90$  °C was determined as the optimal temperature for SIM-3a dehydration.





Figure 14 – Correlation between  $\Delta w$  and  $\Delta T$  over four cycle testing of SIM-3a in Gen3 rig

As in the long cycle, Figure 14 illustrates the almost linear correlation between instantaneous  $\Delta w$  and  $\Delta T$  for the four repeated cycles. Although there are slight differences for each cycles line however, all of them are in close approximation and can therefore be generalized to simulate THS performance according to the  $\Delta w$  of the process air. Obviously, it would be of benefit to have a considerable amount of repeated cycles (~20 cycles) to truly assess the cyclic performance of the process and draw a more realistic operating line, unique for a certain design/absorbent, indicating the achievable temperature lift for a specific change in  $\Delta w$ . In

addition it should be noted that under real UK winter climate conditions it may not be possible 647 to supply high moisture levels to the absorbent which could lead to poor system performance. 648 For instance an ambient temperature,  $T_a = 10$  °C and  $RH_a = 50\%$  would correspond to a  $w_a =$ 649 650 3.77 gr/kg. Under these psychrometric conditions, even if the air is saturated to 100% RH,  $w_a$ will be limited to 7.5 gr/kg. This is the maximum moisture amount that could be supplied to the 651 652 absorbent and, even if all the moisture were fully absorbed, the theoretical maximum temperature lift achievable would  $\Delta T_{peak} < 20$  °C (based on the operating line proposed earlier). 653 Therefore in real applications, especially under severe winter conditions, pre-heating the air 654 before entering the humidifier by some solar source or recycling a certain amount of the outlet 655 air from the heat storage reactor could significantly improve heat storage performance by 656 increasing  $w_a$  considerably. Further studies on this concept are planned as next step of this 657 658 research.

### 659 6. Conclusions

In this study the thermal performance of three different absorbents were experimentally investigated using two different testing rigs. The aim was to both compare material performance and rig design/performance. The main findings were;

• SIM-3a provided the best performance in terms of thermal performance and multi-cyclic ability. Although Zeolite also presents good thermal properties it fails due to its high regeneration temperature requirement. SIM-3a also has a lower cost and greater potential for commercial usage.

SIM-3f unexpectedly showed relatively poor performance against the other absorbents. V-LiNO<sub>3</sub> was added to increase the performance of SIM-3a, however this was not successful.
The Gen3 test rig provided improved performance over Gen2. The use of perforated tubes enhances both moisture and heat transfer allowing for higher and steadier temperature lift

- during discharging. The tubes increase mass transfer into the absorbent, with minimal
   resistance, which is one of the current challenges in 'open' THS systems.
- An air mass flow rate of 0.015 kg/s was optimal as it provided the highest temperature lift.
- There is a direct and linear correlation between the amount of water vapour supplied to the
- absorbent and the temperature lift. This shows that low inlet air temperature limits the water
- vapour that can be added to the air. This is critical in winter conditions where storage is most
- required. Use of solar energy (if available) or circulating some of the output heat during the
- discharging process to preheat the incoming air would improve heat storage performance.

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