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- **1** Analysis of the Hygrothermal Functional Properties of Stabilised Rammed Earth Materials
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10 Abstract

Suitable experimental methodologies for determining the hygrothermal properties of 11 stabilised rammed earth (SRE) materials have been presented along with comparative 12 experimental data for three different SRE mix designs with parametric analysis of the 13 14 influence of these variables on material function. Higher bulk porosity corresponds to reduced volumetric heat capacity (C), but increased sorptivity (S) and vapour permeance (W). Since 15 16 bulk porosity and void size distribution (VSD) are interdependent variables, it follows that for constant particle size distribution (PSD) and compaction energy an increase in porosity results 17 in an increase in the mean pore radius, \bar{r} for a material. This explains why the magnitude of 18 liquid/vapour transfer (S and W) terms are inversely related to the hygroscopic moisture 19 capacity, ξ since the capillary potential, Ψ will increase when the mean pore diameter 20 decreases. The implications are that the hygrothermal properties of SRE materials can be 21 designed and predicted by manipulating particle size distribution and compaction energy. 22 23

Keywords: hygrothermal; porous materials; stabilised rammed earth; heat & mass transfer
and storage

26

27 Nomenclature:

- $V_{\rm T}$ = total volume
- V_s = volume of solid
- V_v = volume of void
- V_a = volume of air
- $V_m = \text{molar volume}$
- $p_v =$ vapour pressure
- $p_{sat} = saturation vapour pressure$
- p_{sat}^* = saturation vapour pressure above a flat surface
- $P_a = \text{total air pressure}$
- $P_w =$ total water pressure
- r = pore radius
- r_{crit} = critical pore radius
- \overline{r} = mean pore radius
- T = thermodynamic temperature (K)
- $\eta = viscosity$
- γ = surface tension
- ϕ = relative humidity ($0 \le \phi \le 1$)
- 45 RH = relative humidity % (ϕ *100)
- θ = relative moisture ($0 \le \theta \le 1$)
- θ_r = residual moisture content
- θ_c = capillary saturation moisture content
- θ_{AEV} = air entry value moisture content
- θ_s = saturation moisture content
- $\rho_w = \text{density of water } (\text{kg/m}^3)$

- $\rho_v = \text{density of water vapour (kg/m^3)}$
- g =gravitational constant
- h = height
- $g_{v, air}$ = rate of water vapour diffusion through air
- D = diffusion coefficient for water vapour in still air (m²/s)
- $C_v = \text{mass concentration of water vapour (kg/m³)}$
- M_w = molar mass of water (kg/kg mol)
- R_o = the universal gas constant (J/kg mol K)
- $m_w = \text{mass of water (kg)}$
- A = area
- G = water vapour flow rate (kg/s)
- W = water vapour permeance (kg/m² s Pa)
- i = cumulative volume of absorbed water per unit inflow surface area (mm³/mm²)
- *t* = time

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$$S =$$
sorptivity (mm/min^{-0.5})

- $\xi = hygroscopic$ moisture storage function
- Ψ = capillary potential
- λ = thermal conductivity (W/m K)
- λ^* = moisture content-dependent thermal conductivity (W/m K)
- q_{sens} = sensible heat flow (W/m²)
- $q_{lat} = \text{latent heat flow (W/m^2)}$
- w = reference moisture content (kg/m³)
- $g_v =$ rate of water vapour transfer (kg/s m²)
- $h_e = \text{specific latent enthalpy of evaporation/condensation (J/kg)}$
- S_r = degree of saturation (or saturation ratio)
- $m_f = \text{moisture factor}$

78 c_p = specific heat capacity at constant pressure (J/kg K)

79 c_p^* = moisture content-dependant specific heat capacity at constant pressure (J/kg K) 80 ϖ = relative mass fraction

81

82 **1** Introduction

83 Approximately one half of the world's population are said to live or work in an earth building [1] and 84 it has long been mooted that earth materials have the ability to provide superior levels of indoor thermal comfort, e.g. [2, 3, 4]. Stabilised rammed earth (SRE) is the modern practice of a traditional 85 construction technique and is typically achieved by the addition of $\leq 10\%$ Portland cement to subsoil 86 87 and dynamic compaction (ramming) of the mixture into temporary formwork. It provides a low embodied energy material for rapid construction on-site. Its modern day use is widespread across 88 89 Australasia, North America, Asia, and parts of mainland Europe such as Spain, Germany and France and increasingly Great Britain. Since earth is a porous, hygroscopic material that contains active clay 90 91 minerals, it is expected that the walls absorb water vapour from the air when relative humidity increases and release this moisture when the humidity falls. As it is usual practice to leave earth walls 92 93 exposed to the interior of the building, the availability of combined thermal and hygric buffering (i.e. 94 passive air conditioning) will be maximised when compared with other materials such as brick, timber or concrete that are often covered over with more insulating and less permeable coverings, e.g. varnish 95 96 and paints.

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The functional properties of SRE that can be used to describe its hygrothermal behaviour are the moisture storage function, vapour permeability, liquid conductivity, thermal conductivity, and specific heat capacity. Samples of three SRE mix designs were manufactured and tested to determine these functional properties and the results compared.

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The objective of this paper is to investigate how the hygrothermal properties of SRE materials
 can be experimentally measured and how these functional properties are influenced by the

variable mix design parameters of the material. The aim is to test the hypothesis that 105 hygrothermal properties can then be predicted and designed through correspondence with mix 106 design parameters. SRE materials can be characterised as multiphase granular composites 107 108 whose particle size distribution (PSD) and particle packing efficiency largely determine the geometry of their matric structure. The term stabilisation refers to the application of a process 109 110 and/or additive component that enhances the cohesion, Young's modulus or another physical property [5-7]. By far the most common forms of stabilisation are i) dynamic compaction and 111 112 ii) addition of hydraulic binders, e.g. cementicious materials. As with most granular soils, dynamic compaction close to the Proctor optimum moisture content increases the inter 113 114 particle friction/interlock whilst reducing the bulk porosity. The addition of hydraulic binders (commonly <10% Portland cement) increases the internal cohesion of the material and 115 enhances durability and toughness [5-9]. Since hardened cement paste bonds particles 116 together by surface adhesion between the paste and particle surfaces (interfacial transition 117 zone), cement stabilisation is most effective on granular soils [8-10] where the specific 118 119 surface area per unit mass is lower and the greater absence of cohesive materials is less able to interfere with the interfacial transition zone. 120

121

122 2 Specimen Preparation

The characterisation of SRE material composition can easily be approximated using the 123 geotechnical soil model. The particle size distribution for SRE must normally fall within 124 designated upper and lower limits resulting in a wide range of achievable particle packing 125 efficiencies and associated bulk porosity/dry density and void size distribution (VSD), as 126 127 explained extensively in the authors' previous research [11-13]. By using an established technique of blending characterised soil constituents (14-6.3mm gravel, 5mm down medium 128 grit sand, silty clay) and matching the net PSD to the defined upper/lower limits, the authors 129 can maintain the parameters of aggregate mineralogy, particle angularity and clay mineralogy 130

as constants whilst keeping PSD as the single variable. SRE specimens were prepared as one litre cylinders (3 compaction layers), 1/3 litre discs (1 compaction layer), and 300 x 300mm slabs (1 compaction layer). All were stabilised by compacting at OMC using a constant energy of 596 kJ/m³ and the addition of 6% wt CEM IIa class Portland cement, followed by air curing for a minimum of 28 days at 20° C (\pm 2° C) and 75% RH (\pm 5%) in an environmental chamber.

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3 Moisture Sorption and Storage

The assumption here for hygrothermal materials is that a representative microstructure of 139 porous media has a total volume (V_T) which consists of solid state matter (V_s) and fluid-filled 140 141 void (V_v) , where $V_T = V_s + V_v$. Under atmospheric conditions, when the material is dry the voids are filled with air $(V_v = V_a)$ and when saturated the voids are filled with water $(V_v = V_w)$. 142 Clearly, when moisture enters a dry or unsaturated continuum it must displace air from the 143 moment it crosses the boundaries defined by V_T ; a process referred to as 'absorption'. 144 Absorbed moisture vapour may also be 'adsorbed' to the internal surfaces by van der Waals 145 forces. Absorbed moisture may be classified into one of three domains (hygroscopic, 146 capillary, and gravitational) depending upon i) its phase when it enters V_T , and ii) its strength 147 of electrostatic attraction. Hygroscopic moisture is absorbed in the vapour phase, capillary 148 moisture is absorbed in the liquid phase, and gravitational moisture is liquid that is absorbed 149 when the capillary potential in the pore network is zero (i.e. super saturation). 150

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Although the classification of absorbed moisture (determined by its phase upon entry) cannot change, its phase once inside V_T can change, e.g. condensing from vapour to liquid. This is chiefly governed by internal void geometry and electrostatic surface charge for a given temperature and partial vapour pressure. Theoretically, the saturation vapour pressure above a flat surface of liquid water (p_{sat}^* , when $r = \infty$) is dependent upon the pressure applied (ΔP_a) to

that liquid by a surrounding gas, in this case air. For a given ΔP_a , the saturation vapour 157 pressure becomes $p_{sat} = p_{sat} * e^{V_m \Delta P / R_o T}$ [14]. Furthermore, by curving the surface of the water 158 to a known radius, r a pressure change (negative for water) occurs where $\Delta p_{\text{sat}} = 2\gamma/r$. 159 Therefore, we can see that the saturation vapour pressure of liquid water held inside a pore of 160 radius r (and having a contact angle α) is greater than that of a flat surface, i.e. $p_{sat} > p_{sat}^*$. 161 This of course leads to Kelvin's Equation, $p_{sat} = p_{sat}^{*} e^{-2\gamma V_m / rR_o T}$ where molar volume of water 162 ~ 18 ml at STP [14]. In the case of hygroscopic moisture (vapour phase) of known partial 163 pressure, p_v that has been absorbed by a pore, Kelvin's equation can simply be rearranged to 164 find the 'critical pore radius' (r_{crit}) assuming $p_v = p_{sat}$. At this point moisture vapour condenses 165 inside the pore to restore thermodynamic equilibrium. Obviously, where radii vary within 166 complex pore structures it follows that vapour condenses to fill the pore with liquid when r < r167 168 r_{crit} , and visa versa.

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Figure 1 shows the wetting/drying sorption isotherms for a typical hygrothermal material, 170 171 correlating relative moisture content, θ with absorbed moisture domains. As with liquid sorption, hysteresis typically occurs between the relative moisture content, θ at a given 172 173 humidity, φ due to the influence of electrostatic potential on the porous material inside surfaces. As relative humidity increases from zero, single layer adsorption and then multi 174 175 layer adsorption of water vapour molecules occurs within the pore structure of the material. 176 Metastable groups of adsorbed water vapour molecules can spontaneously nucleate into a liquid water meniscus that is in equilibrium with the relative humidity for a given pore radius, 177 178 as predicted by the Kelvin equation. In this way, hygroscopic moisture can be stored in liquid phase inside the porous material. Kelvin's equation can be used to calculate the theoretical 179 critical pore radius in which water vapour condenses in relation to the relative humidity. The 180 181 validity of Kelvin's equation applies to the portion of a sorption isotherm where capillary condensation will occur in pore radii sufficient to permit thicknesses greater than multi 182

molecular layers, i.e. droplets. This typically occurs at $\varphi \approx 0.5$, although the occurrence of 183 capillary potential-induced liquid moisture flow is typically not considered until $\varphi > 0.8$ [15] 184 (refer to value θ_{80} , Figure 1). At the hypothetical point when $\varphi \rightarrow 1$, the transition from 185 hygroscopic to capillary domain occurs and is defined as the residual moisture content, θ_r . For 186 187 modelling purposes, however, a 'kick point' moisture content can be specified to indicate the maximum hygroscopic moisture content since that can be readily determined experimentally, 188 189 e.g. normally 95 or 98% RH [15, 16]. Above this level pressure plate apparatus can be used for relative humidity at saturation. When θ is in the capillary domain, moisture transport is 190 dominated by capillary potential, Ψ and the microstructure is referred to as 'unsaturated' (as 191 in soil mechanics), refer to Figure 2. During wetting, absorption will continue until capillary 192 saturation θ_c at which point the ambient air pressure $P_w = P_a - (2 \gamma / r + \rho_w gh)$, for the 193 supported mass of water inside the pore structure (where g is the gravitational constant) [14]. 194 Obviously, if $\theta_c \ll \theta_s$ (fully saturated) then additional moisture can be absorbed without 195 196 capillarity (e.g. pressure differential, gravity etc), some of which can be supported by remaining net surface charge in the pore network surfaces. Thus, on the drying curve the 197 maximum capillary moisture content is determined by the air entry value to find θ_{AEV} . At 198 'super saturation' (> θ_{AEV}) the force of gravity on the additional mass of the non-capillary (or 199 gravitational) moisture is greater than the attraction of the remaining net surface charge inside 200 201 the pore structure.

202

The sorption and desorption isotherms were determined for representative samples of each rammed earth mix recipe. SRE disc specimens were split into large fragments ($V_T \approx 15$ ml) and oven dried to constant mass at 105° C. An array of five sealed desiccators was prepared, each containing a different saturated salt solution and stored at an ambient air temperature of 23°C ± 0.5°C in order to provide a wide range of stable relative humidity environments (see Table 1). The dry specimens were progressively placed in each of the desiccators, in order of

increasing humidity, and permitted to absorb moisture vapour until constant mass was 209 achieved (normally > 3 days), defined as <0.1% Δ wt/day [17]. Samples were then fully 210 immersed in distilled water for 24 hours and the saturated mass recorded to find θ_c , but θ_r can 211 212 only be interpolated since it occurs at $\varphi \rightarrow 1$. The capillary saturated specimens were then progressively placed in each of the desiccators in order of decreasing humidity. In this manner 213 214 both the sorption and desorption isotherms were determined. The relationship between the moisture content of a porous material and the relative humidity of the surrounding 215 environment is described by the moisture storage function (MSF). It is used to calculate the 216 partial pressure of a water vapour gradient for water vapour diffusion as well as the capillary 217 potential gradient for liquid water conductivity (see part 1). 218

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220 **4**

Water Vapour Transport

It is apparent that the fluid transport mechanism in porous materials is not simply defined by its domain classification. Once fluid has entered the porous medium V_T , the intrinsic conditions of the pore network will determine i) fluid phase, and ii) its associated transport mechanism(s). To elucidate, absorbed hygroscopic moisture (from vapour) will subsequently be adsorbed by internal surfaces, condense, or diffuse. Absorbed capillary moisture (from liquid) will either flow or vaporise. The intrinsic properties that determine these conditions include pore radius, pore geometry, surface charge, and surface temperature.

228

Water vapour can enter porous materials through pore openings at the surface and liquid water inside the material can evaporate. The material's granular skeleton reduces the available cross-sectional area of air for vapour diffusion and the complex spatial connectivity of the pore spaces increases path lengths, providing additional resistance. For pores with smaller diameter, the mean molecular free path of the water vapour molecules approaches or exceeds the pore diameter. In this case, pore wall collisions and van der Waals forces between the water vapour and pore surface dominate molecular movement, i.e. Knudsen diffusion. Also, water vapour molecules that are adsorbed to the walls of the

pores inside the material, either in a single layer or as multiple layers, can move along the surface by

surface diffusion. These phenomena are illustrated in Figure 3.

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239 The rate of water vapour diffusion in still air can be described by Fick's law:

240
$$g_{v,air} = -D \frac{\partial C_v}{\partial x}$$
(1)

241 This equation can be expressed in terms of water vapour partial pressure using the ideal gas law:

242
$$C_{\nu} = \rho_{\nu} = \frac{p_{\nu}M_{w}}{R_{\rho}T}$$
(2)

The rate of water vapour flow through a porous specimen can be determined using the wet 243 cup/dry cup method [18] in a temperature and humidity controlled environmental chamber, 244 see Figure 4. By using a saturated salt solution for the 'test' vessel, a vapour pressure gradient 245 was imposed across the sample thickness thus inducing diffusive mass transfer. The 246 specimen sides were coated with a 2-part epoxy resin and sealed into the cups using silicone 247 sealant to ensure vapour tightness. For the SRE specimens a 'test' solution of Potassium 248 Nitrate KNO₃ (94.0% RH) was used in the cup (i.e. a 'wet' cup) and the climate chamber set 249 to 23°C and 53.5% RH, see Table 1. The actual air temperature and relative humidity were 250 logged for the duration of the test using Tiny Tag sensors with an accuracy of \pm 0.4 °C and \pm 251 252 3 %RH. Specimen mass increase was determined gravimetrically, and the quantity of 'test' solution was sufficient to permit test periods of between 2 and 3 weeks. The absorbed mass 253 254 (Δm_w) increased linearly against the elapsed time (t), and the slope $\Delta m_w/t$ gave the water vapour flow rate, G through the specimen in kg/s, see Figure 5. The water vapour permeance 255 was then calculated from: 256

$$W = \frac{G}{A \cdot \Delta p_{v}} \tag{3}$$

258 Where A = specimen inflow surface area (m²), and Δp_{ν} = water vapour pressure difference 259 across the specimen (Pa) which was calculated from the mean of the measured temperature 260 and relative humidity over the course of the test. 261

262 **5 Liquid Water Transport**

Previous research has shown that bricks, stone, and SRE materials have been found to obey 263 the $i/t^{0.5}$ linearity rule demonstrating dependence upon the $\gamma/\eta^{0.5}$ relationship [13, 19-21], i.e. 264 capillary potential is the motivational force for flow in the unsaturated state. Theoretically, the 265 sharp wet front approximation can be used to model absorption and desorption of capillary 266 moisture and the associated transfer rates [13, 20]. Experimentally, the gravimetric 267 measurement of absorbed volume per unit inflow surface area, $i (mm^3/mm^2)$ is measured 268 using test specimens that are partially immersed to a constant a depth of $5mm \pm 1mm$. Pre-test 269 conditioning and actual testing of the specimens were performed by the authors in a large 270 environmental chamber at $23^{\circ}C \pm 1^{\circ}C$ and $50\% \pm 5\%$ relative humidity. In SRE materials, 271 increasing the cementicious binder content resulted in an increase in bulk porosity and hence 272 an increase in the sorptivity, S. More interestingly this was found to give higher initial rates of 273 274 suction but which decreased very sharply over time due to the moisture-content dependent nature of the capillary potential [13]. It is hypothesised that since n and \overline{r} are interdependent 275 in porous granular media, then a reduction in both (caused by changing PSD and/or 276 compaction energy) would increase Ψ (due to smaller \bar{r}) but reduce ξ (due to lower porosity). 277 Hence, the rate of flow reduction over time, as a result of $\Psi(\theta)$, is higher when changes to 278 material pore structure result in $\Delta \theta_c$ being negative. The experimental data for SRE materials 279 has been presented elsewhere [13, 21], and partly in Table 2 for comparison. 280

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6

Heat Transfer and Storage

Within a porous building material, heat transfer can occur through a number of mechanisms (see Figure 6). Firstly, there is conduction, which occurs primarily through the material's granular skeleton, which in the case of SRE consists of hydraulically-bound mineral aggregate particles and clays. Heat transfer will be enhanced by the introduction of water into the voids

between particles as the thermal conductivity of water is an order of magnitude higher than 287 air, and conduction at inter-particle contact points is augmented by menisci formation. 288 Localised radiative and convective heat transfer will also occur between particles within the 289 290 matric structure and these are assumed to be included within the continuum-level moisture content dependent thermal conductivity, λ^* (W/m K) [11]. The dry state and moisture-291 dependant thermal conductivity (λ^*) were measured using a heat flow meter apparatus to ISO 292 8301 [11]. Moisture factor (m_f) the slope of the $\lambda : S_r$ graph and was determined by linear 293 regression. such that: 294

295
$$\lambda^* = \lambda \left(1 + S_r m_f \right) \tag{4}$$

The moisture content-dependant specific heat capacity, c_p^* was calculated as the sum of the heat capacities of the constituent parts, weighted by their relative mass fractions, σ , as shown in Equation 2 [12, 22].

$$\rho_{bulk}c_p^* = \rho_{dry} \left(\overline{\omega}_{sand} c_{sand} + \overline{\omega}_{gravel} c_{gravel} + \overline{\omega}_{clay} c_{clay} + \overline{\sigma}_{cem} c_{cem} \right) + wc_w$$
(5)

The results from these tests have previously been presented [11, 12] and are shown in Table 2 for direct comparison of all hygrothermal properties between each of the materials.

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7 Parametric analysis of hygrothermal properties

Table 2 shows the hygrothermal functional properties for each of the three SRE materials. The 304 parametric difference between each material is the particle size distribution which, since 305 compaction energy and solid phase properties are constant, results in variation in packing 306 efficiency and hence i) bulk porosity and, ii) void size distribution. Clearly dry density and 307 bulk porosity are inversely related and so higher porosity results in reduced volumetric heat 308 capacity (C), but increases sorptivity (S) and vapour permeance (W). These broad trends are 309 somewhat predictable, and the new data presented here can be used by other researchers in 310 transient hygrothermal modelling of SRE materials. Interesting trends occur when one 311 considers the intricacies of inter-particle contact, void size distribution and pore network 312

tortuosity brought about by particle packing efficiency. Moisture factor m_f , for example,

314 represents the sensitivity of a material's thermal conductivity to increasing degree of

saturation and is not simply related to porosity [11, 12]. Much more research is needed to

316 understand how heat transfer occurs in porous granular materials.

317

318 Whilst the uncertainty in the measurements made for the tests were small (balance accurate to 319 +/-0.01g, stop watch accurate to 1s) and the test environments were closely controlled and 320 monitored (temperature better than +/- 1°C and RH better than +/-3%), simply propagating these errors may underestimate the uncertainty of the results. Galbraith [23] has shown that, 321 322 for identical materials, different laboratories can produce results that vary in excess of +/-20% of the mean vapour permeability result for particle board. This was attributed to systematic 323 error in the tests as evidenced by the large bias between individual laboratories. Assuming 324 that the tests are carried out carefully, a confidence interval of +/-5% should be achievable 325 [23], however the properties of rammed earth specimens are known to vary between samples 326 327 and wider variation may be expected (authors have found strength tests to typically vary by +/-20%). Further testing is therefore required to determine the accuracy of the results, 328 however, while the moisture storage function for the three materials described here may be 329 330 deemed similar, it is reasonable to attribute significant differences in the permeability results. 331

The sorption isotherm in Figure 7 shows the wetting and drying curves for each of the three SRE materials. The point θ_r is difficult to measure experimentally since by definition it occurs at $\varphi \rightarrow 1$. Therefore, the important transitional point θ_c has been found and the portion of the isotherm shaded in grey (between >95% RH - 100% RH) is interpolated for completeness. Although at scale the moisture storage curves are very similar a degree of hysteresis occurs between wetting and drying as a result of changes to the net capillary potential as described previously. The gradient of the linear section of the moisture storage curves is used to

determine the hygroscopic moisture capacity for absorption (wetting), ξ_a and for desorption (drying), ξ_d , the values for which are given in Table 2. A particular portion of the isotherm that is of interest in relation to building physics is that which occurs in the RH range that is defined as the indoor comfort zone, i.e. between 40 and 70% RH [24].

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344 Figure 8 highlights disparities that occur between the wetting/drying moisture storage curves for respective SRE materials where the indoor comfort range (above) is shaded. The total 345 hygroscopic moisture storage capacity of SRE materials appears to vary by a small amount in 346 relative terms. Interestingly, in terms of material functional properties the moisture storage 347 capacity across the range appears to inversely relate to porosity. The 433 material, for 348 example, exhibits the highest hygroscopic moisture storage capacity (across the range) and 349 350 correspondingly the highest $\Psi(\theta)$, however this material also has the lowest porosity and vapour permeability. It is assumed that the surface properties of the solid phase material 351 components are constant and since θ never approaches θ_r (always hygroscopic domain), the 352 capacity for moisture vapour storage across a given RH range must be determined by the 353 overlap between VSD and critical pore radii, as defined by Kelvin's equation. This simple 354 relationship, however, relies upon the significant assumption that porosity is a constant. In 355 porous granular materials, PSD and compaction energy effectively determine the particle 356 packing efficiency. Crucially this suggests that bulk porosity and mean pore radius \bar{r} are 357 interdependent variables for porous granular media; increasing packing efficiency will 358 increase the vapour storage function whilst decreasing transfer rates (sorptivity and vapour 359 permeability) and visa versa. The implications are that since VSD and \bar{r} can be controlled by 360 compaction energy and PSD, the hygrothermal functional properties of SRE materials can be 361 designed using this technique, e.g. a 703 mix would sacrifice moisture storage capacity in 362 favour of increased moisture transport rates. 363

364

When considering the use of hygrothermal materials for relative humidity buffering in 365 buildings it is important to consider the response rates of the material to changes in ambient 366 relative humidity. Previous research has drawn direct comparisons between water vapour 367 absorption rates $(g/m^2 s)$ for different materials [25] with the premise that higher values 368 indicate superior buffering ability. The fundamental weakness with this approach is that rather 369 370 than buffering, this data provides the maximum rate since as moisture is absorbed i) the vapour pressure differential decreases (the driving force for absorption rate) towards zero as 371 equilibrium is approached, and ii) the internal mass transfer rates slow down as θ increases. 372 This relationship produces the characteristic w:t curve where $\Delta w \rightarrow 0$ as $\Delta P \rightarrow 0$ 373 374 (thermodynamic equilibrium). Whilst it is not possible to use experimental data of individual functional properties to directly compare moisture buffering capacity between materials, 375 hygrothermal transient models such as WUFI can simulate the effects of moisture buffering 376 377 by coupling mass storage and diffusion functions, and then solving the mass balance equations. 378

379

380 8 Conclusions

Suitable experimental methodologies for determining the functional hygrothermal properties 381 382 of SRE materials have been identified. Comparative experimental data has been presented for three different SRE mix designs enabling parametric analysis of the influence of these 383 variables on hygrothermal properties. Higher bulk porosity corresponds to reduced volumetric 384 heat capacity (C), but increased sorptivity (S) and vapour permeance (W). Since bulk porosity 385 and VSD are interdependent and are largely controlled by PSD and compaction energy, it 386 follows that decreased porosity results in a decrease in \overline{r} for a given material (constant PSD) 387 388 and particle geometry). This is consistent with experimental observations of increased capillary potential coupled with decreased permeability. The variation in vapour absorption 389 capacity is consistent with the latter observation since capacity appears to increases with 390

capillary potential and is inversely related to bulk porosity. However, at total hygroscopic 391 storage capacity appears to vary little as a result of SRE mix parameters whereas response 392 rates can vary significantly. This is perhaps the key to understanding the use of hygrothermal 393 394 materials for relative humidity buffering in buildings because the fabric vapour storage capacity will typically be more than sufficient in relation to the volume of air inside a room. 395 The opportunity for SRE materials to perform well in this regard is related to optimising their 396 response rate to match the anticipated fluctuations in vapour pressure gradients. A 397 fundamental understanding of hygrothermal behaviour can be combined with an 398 understanding of the functional properties of hygrothermal materials, including experimental 399 approaches to quantifying these properties. The next step is to verify this predictive approach 400 by numerically simulating the hygrothermal behaviour of SRE walls under known 401 indoor/outdoor climatic conditions and then comparing the predicted material responses with 402 experimental measurements. 403

404

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408

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458	Figure	Captions

4	5	9

460

461	Equation critical pore radii
462	Fig 2 - Capillary potential: relative moisture content graph with corresponding moisture
463	domains
464	Fig 3 - Mechanisms of vapour diffusion in porous granular materials
465	Fig 4 - Experimental apparatus for determining water vapour permeability (left) and water
466	vapour absorption (right)
467	Fig 5 - Graph showing upper/lower range of mass transfer rates for each SRE material in a
468	vapour permeability test
469	Fig 6 - Heat and mass transfer in porous granular materials
470	Fig 7 - Sorption isotherm showing wetting (sorb) and drying (desorb) curves for the three
471	SRE materials
472	Fig 8 - Indoor thermal comfort portion of the sorption isotherm for comparative analysis of

Fig 1 - Water vapour sorption isotherm illustrating relative moisture contents and Kelvin

473 wetting/drying curves between SRE materials

Table 1 - Saturated salt solutions and associated partial pressure variables

Salt solution	RH (%) at 23°C
Magnesium chloride	32.90 ± 0.17
Potassium carbonate	43.16 ± 0.36
Magnesium nitrate	53.49 ± 0.22
Sodium bromide	58.20 ± 0.42
Sodium chloride	75.36 ± 0.13
Potassium nitrate	94.00 ± 0.60



	P <i>dry</i>	п	Thermal Properties				Hygric Properties				
mix			С	λ	m_f	λ*		S	W	ξa	ξa
	kg/m ³	-	MJ/m ³ K	W/m K	-	W/m K		mm/min ^{0.5}	kg/m ² sPa	kg/kg	kg/kg
						$S_r = 0$	$S_r = 1$	-			
433	2120 ^a	0.239 ^a	1.754	1.010 ^a	0.802	1.010	1.820	1.487 ^b	1.56E ⁻¹⁰	23.20	31.56
613	2020 ^a	0.273 ^a	1.728	0.833 ^a	0.643	0.833	1.369	2.117 ^b	3.23E ⁻¹⁰	28.71	19.19
703	1980 ^a	0.302 ^a	1.719	0.866 ^a	0.955	0.866	1.693	2.700 ^b	4.79E ⁻¹⁰	13.93	21.30
178	^a [8]										

Table 2 - Hygrothermal properties of SRE mix recipes 477

478 479

^a [8] ^b [10]