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1 **A hygrothermal modelling approach to water vapour sorption isotherm design for**
2 **mesoporous humidity buffers**

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10
11 **Abstract**

12 This paper describes the development of a design technique using hygrothermal numerical
13 modelling for top-down predictive design and optimisation of water vapour sorption
14 isotherms to match any humidity buffering application. This was used to inform the design
15 and synthesis of two new mesoporous silica (MS) materials suitable for specific applications.
16 To validate the technique, the new materials were experimentally assessed using gravimetric
17 dynamic vapour sorption (DVS). The experimental isotherms closely matched the optimised
18 isotherm predictions from the design stage, and a positive correlation was observed between
19 the rate of change in adsorbed water content, Δw and the time taken to exceed the permissible
20 upper limit of humidity, $\varphi_{i,U}$ in a closed environment. A positive non-linear correlation was
21 determined between the interior volumetric moisture load, ω_{ml} and the mass of adsorbent
22 required to fully achieve humidity buffering between specified lower/ upper limits ($\varphi_{i,L}$ and
23 $\varphi_{i,U}$). The kinetics of water vapour sorption/ desorption were found to have general agreement
24 when using the current hygrothermal numerical model. Current hygrothermal models appear
25 to significantly underestimate the rate of adsorption/ desorption in rapid-response mesoporous

26 silica type materials. This is perhaps largely due to the current lack of consideration for
 27 scanning curve prediction within hysteresis loops and so is a priority for future research.

28

29 **Keywords:** hygrothermal modelling; water vapour isotherm; isotherm design; humidity
 30 buffering

31

32 **Nomenclature**

| | | | |
|----|------------------------------------|--|--------------------------------|
| 33 | ρ | Bulk density | kg/m ³ |
| 34 | c_p | Specific heat capacity | J/(kg K) |
| 35 | $\lambda(\mathbf{w})$ | Moisture-dependent thermal conductivity | W/(m K) |
| 36 | φ | Relative vapour pressure (p_v/p_{sat}) | - |
| 37 | \mathbf{n} | Bulk porosity | m ³ /m ³ |
| 38 | $\mathbf{w} = \mathbf{f}(\varphi)$ | Water vapour sorption isotherm | kg/m ³ |
| 39 | $\mu(\varphi)$ | Water vapour diffusion factor | - |
| 40 | $\mathbf{D}_w(\mathbf{w})$ | Liquid water diffusivity | m ² /s |
| 41 | RH | Relative humidity; where $\varphi \cdot 100$ | % |
| 42 | ω_{ml} | Volumetric moisture load | g/h/m ³ |
| 43 | H | Total enthalpy | J/m ³ |
| 44 | h_v | Latent heat of phase change | J/kg |
| 45 | t | Time | s |
| 46 | T | Temperature | K |
| 47 | δ_p | Vapour permeability | kg/(msPa) |

48 **Suffixes:**

| | | |
|----|---|-------------|
| 49 | i | interior |
| 50 | e | exterior |
| 51 | L | lower limit |
| 52 | U | upper limit |

53 **1. Introduction**

54 Regulation of the psychrometric variables within pre-defined upper/ lower limits, to match the
55 requirements of ‘closed environments’ (e.g. cars, aircraft, buildings, incubators, laboratories,
56 archives, etc.) accounts for the vast majority of global energy consumption and all associated
57 emissions [1-3]. The study of hygrothermics considers an enclosed volume of air in which the
58 psychrometric conditions are isolated from the exterior environment by limiting the exchange
59 of heat, air, and moisture. In relative humidity (RH) buffering applications desirable
60 hygrothermal behaviour is a material’s capacity for simultaneous buffering of fluctuations in
61 energy (air enthalpy) and mass (water vapour) concentration with respect to equilibrium
62 moisture content [4, 5]. Some examples of moisture buffering applications in closed
63 environments are preventing mould formation [6-9], building fabric damage [10-12],
64 regulating thermal comfort for human activities [13-17], and energy efficient retrofit of
65 existing/ older buildings [18-20]. On the other hand, disregarding RH buffering from
66 hygrothermal materials lead to energy and cost penalties. These are caused by relying on
67 continuous use of air conditioning (normally oversized) regardless of occupation, reducing the
68 efficiency of the systems and increasing the energy consumption [21-23]. Advanced
69 mesoporous materials could be then used to fully buffer fluctuations in psychrometric
70 variables by designing them to have hygrothermal properties compatible with the pre-defined
71 upper/ lower limits of any closed environment.

72

73 Hygrothermics studies the coupled phenomena in porous solids that occur as a result of
74 adsorption, diffusion, and desorption of heat and moisture (liquid and vapour phases). The
75 moisture storage function is one of several hygrothermal functional properties, where $w = f(\phi)$
76 defines the non-linear relationship between the mass of adsorbed water and the ratio of vapour
77 pressure to saturation vapour pressure; known as a sorption isotherm when at constant
78 temperature. The maximum value for w depends on n , corresponding to total pore volume,

79 whilst $\lambda(w)$ describes the positive dependency of thermal conductivity on w . The summation
80 of c_p for the adsorbent and adsorbate describe stored energy, whilst substantial heat transfer
81 can occur due to both heat of adsorption and evaporation/ condensation of the adsorbate
82 during transport. In the hygroscopic domain, the (Fickian) diffusion coefficient is a function
83 of relative vapour pressure, $\mu(\phi)$ as a result of pore network constriction by condensation
84 filling. In the capillary domain, the water diffusion coefficient is a function of water content,
85 $D_w(w)$ [24, 25]. This leads to the well-known contra- and counter flow mass transport
86 scenarios in hygrothermics (see Fig. 1) [26, 27].

87

88 The morphology and volume of the pore network in mesoporous silicas can be easily
89 modulated through the synthesis process (using surfactants as a template for polycondensation
90 of silica species) by controlling the temperature [28, 29] and reaction time [30, 31]. This
91 makes them an ideal template material from which to control and synthesise hygrothermal
92 functional properties with respect to RH buffering. Significant interest in these materials has
93 previously focussed on catalysis [32-34], separation [35-37], gas adsorption [38-40], and drug
94 delivery [41, 42]. However, hygrothermics not only has to consider isothermal physisorption
95 but also the temperature-dependency of heat & moisture diffusion and storage, as well as the
96 moisture-dependency of thermal conductivity and heat storage. Hygrothermal models are
97 constitutive and so require bulk-scale functional properties as inputs to represent mesoporous
98 solids. The bulk-scale properties are therefore statistically-averaged representations of the
99 mesopore-scale behaviour. In recent work, two important principles were established for the
100 hygrothermal behaviour of mesoporous solids: (i) an empirical correlation between mesopore
101 diameter and the kinetics of RH buffering [43], and (ii) prediction of the required adjustment
102 to the hygrothermal functional properties of one mesoporous solid in order to duplicate the
103 behaviour of another [20]. However, the relationships between structure (mesopore geometry,

104 physisorption and hysteresis) and properties (hygrothermal functions) are still neither
105 quantified nor fundamentally understood.
106 The aim of this study was to develop a hygrothermal numerical modelling technique that
107 enables top-down predictive design of the ideal water vapour sorption isotherm for any RH
108 buffering application. The parameters for design would be a closed environment of volume, V
109 in which the upper and lower limits for psychrometric variables (T_{\max} , T_{\min} , ϕ_{\max} , ϕ_{\min}) were
110 specified. This technique was developed using three pre-existing materials from a previous
111 study, and then used to inform the synthesis of two new MS; both having hygrothermal
112 properties optimised to suit two different closed environment scenarios. The water vapour
113 sorption isotherms and RH buffering behaviour of these two materials were then assessed
114 experimentally.

115

116 **2. Experimental**

117 2.1. Synthesis and characterization

118 The two new pure silica MCM-41 samples were synthesized from fumed silica as silica
119 source, cetyltrimethylammonium bromide (CTAB) as structure directing agent or template,
120 tetramethylammonium hydroxide (TMAOH) and water. In a typical synthesis, 1.9 g TMAOH
121 and 4.6 g CTAB were dissolved in 34.1 g of distilled water under stirring at 35 °C, following
122 which 3.0 g fumed silica was added to the solution under stirring for 1 h to obtain a
123 homogeneous gel of molar composition $\text{SiO}_2:0.25\text{CTAB}:0.2\text{TMAOH}:40\text{H}_2\text{O}$, which was left
124 to age for 20 h at room temperature. The aged gel mixtures were then transferred into a
125 Teflon-lined autoclave and heated, under static conditions, at 150 or 180 °C, for 48 h. The
126 solid product was then filtered off, washed with water and dried in air at room temperature to
127 yield the as-synthesized sample. The surfactant templates within the as-synthesised sample
128 were removed by calcination (heating ramp rate of 5 °C/min) at 550 °C for 6 h. The final

129 calcined silica samples were designated as MCM-41-x where x is the synthesis
130 (crystallisation) temperature, i.e., 150 or 180 °C.

131

132 2.2. Material Characterisation

133 Powder X-ray diffraction (XRD) analysis was performed using a PANalytical X'Pert PRO
134 diffractometer with Cu-K α radiation (40 kV, 40 mA), 0.02 step size and 50 s step time.

135 Nitrogen sorption isotherms and textural properties were determined at -196 °C using a
136 conventional volumetric technique by a Micrometrics ASAP 2020 sorptometer. Before
137 analysis, the samples were first dried at 130 °C and then outgassed under vacuum at 200 °C
138 for 12 h. The surface area of the materials was determined using the standard Brunauer–
139 Emmett–Teller (BET) method based on adsorption data in the relative pressure (P/P_o) range
140 of 0.05 - 0.2, and pore volume was calculated from the amount of nitrogen adsorbed at P/P_o
141 of ca. 0.99. Pore size distributions were obtained using density functional theory (DFT)
142 analysis of adsorption data.

143

144 For enabling calibration of the hydrothermal modelling technique, three pre-existing
145 mesoporous solids (MS 3.3, 4.7 and 8.3) of varying pore diameter and pore volume were taken
146 from previous research [43] (see Table 1). Pore diameter was controlled during synthesis [43]
147 by using alkyltrimethylammonium ($C_nH_{2n+1}(CH_3)_3N^+$ $n=16$ and $(C_nH_{2n+1}(C_2H_5)_3N^+$, $n=12, 16$
148 [44] with large head group surfactant [45]. Pore geometry and specific surface area were
149 measured in the same study using the Barrett–
150 Joyner–Halenda (BJH) and BET methods with N_2 physisorption, and validated against high
151 resolution transmission electron microscopy (HRTEM) and small-angle X-ray diffraction
152 (SAXRD). The hydrothermal functional properties were determined using modified transient
153 plane source (MTPS), differential scanning calorimetry (DSC) and DVS techniques, the
154 results of which are summarised in Table 1. For this study, the validity of Kelvin's equation

155 was therefore assumed, and the cumulative pore volume histogram obtained from the water
156 isotherms found good agreement with the mean pore diameters determined using the BJH
157 method [43].

158

159 2.3. Design of hygrothermal properties

160 Existing hygrothermal model packages include (but not limited to) WUFI, DELPHIN, HAM
161 and MATCH [46] which have been validated against experimental data over the past 15+
162 years, and addressed as part of the Annex 41 project [47]. Physical models are often used to
163 simulate bulk-scale hygrothermal behaviour and to validate numerical model predictions for
164 heat and moisture transport/ storage [48, 49]. Currently, all hygrothermal numerical models
165 must (as a minimum) accurately represent the following bulk-scale transport and storage
166 phenomena [50]:

- 167 • heat storage in dry materials and any absorbed water
- 168 • heat transport by moisture-dependent thermal conduction
- 169 • latent heat transfer by vapour diffusion
- 170 • moisture storage by vapour sorption and capillary forces
- 171 • moisture transport by vapour diffusion
- 172 • moisture transport by liquid transport (surface diffusion and capillary flow)

173

174 The Wärme und Feuchte Instationär (WUFI) hygrothermal numerical model, WUFI+ v2.5.3
175 (Fraunhofer, Germany), was used for this study [51, 52]. The LHS of Eq. 1 represents the
176 moisture storage function, which is proportional to the derivative of the water adsorption
177 isotherm ($\partial w / \partial \phi$). The transport terms on the RHS of Eq. 1 are described by the divergence of
178 liquid and vapour flow. While vapour pressure ($p_v = \phi \cdot p_{\text{sat}}$), which is the driving potential for
179 vapour flux, is strongly temperature-dependent (saturation pressure $p_{\text{sat}} \sim \exp(T)$), liquid flow
180 is governed by capillary forces which are assumed to be a function of RH only (i.e. from

181 Kelvin condensation). The LHS of Eq. 2 describes the enthalpy of air inside the closed
182 environment, whilst the RHS describes heat transport due to solid conduction and diffusion of
183 heat associated with the specific enthalpy of vapour water.

184

185 Moisture balance: $\frac{dw}{d\varphi} \cdot \frac{\partial\varphi}{\partial t} = \nabla \cdot (D_w \nabla\varphi + \delta_p \nabla(\varphi \cdot p_{sat}))$ Eq. 1

186 Energy balance: $\frac{dH}{dT} \cdot \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + h_v \nabla \cdot (\delta_p \nabla(\varphi \cdot p_{sat}))$ Eq. 2

187

188 2.3.1 Approach to water isotherm design

189 For RH buffering applications it was hypothesised that the optimum isotherm would have the
190 maximum theoretical pore volume and a steep $w: p_v/p_0$ gradient between the upper (φ_{max}) and
191 lower (φ_{min}) limits of a given scenario. Following the same logic, this would imply that all
192 candidate isotherms could be described by a transition from Type I to Type V (inclusive). For
193 a closed environment with internal moisture sources (either fixed, intermittent or variable) the
194 material will fail if the (user-defined) upper limit for indoor RH (φ_{max}) is exceeded.

195 Conversely, if infiltration by exterior air (with much lower moisture content) occurs, the
196 material will fail if the lower limit for indoor RH (φ_{min}) cannot be reached. An optimum
197 sorption isotherm is therefore one that can maintain the fluctuation $\varphi(t)$ between the upper/
198 lower limits (φ_{max} and φ_{min}) of the given scenario. If after subsequent cycles the capacity for
199 moisture storage decays, then after N cycles the fluctuation between φ_{max} and φ_{min} can no
200 longer be maintained and the adsorbent must be fully outgassed for re-use. The initial
201 approach was to (i) generate new isotherm candidates by modifying the isotherms of existing
202 MS 3.3, 4.7 and 8.3 materials (see Section 2.3.3), (ii) conduct sensitivity analysis to correlate
203 the effects of isotherm modification on RH buffering behaviour (see Section 3.1), and (iii)
204 develop a refinement technique to produce an optimum isotherm for any closed environment
205 scenario (see Section 3.2 to 3.4).

206

207 2.3.2 Sensitivity analysis

208 Sensitivity analysis was conducted by selecting the MS materials (MS 3.3, 4.7 and 8.3) from
209 previous research [43]. The fluctuation of $\varphi(t)$ and the material's capacity for humidity
210 buffering were assessed for a closed environment scenario in which the operating limits were
211 $\varphi_{\max} = 0.70$ and $\varphi_{\min} = 0.55$, and the number of moisture loading cycles, $N = 60$. Each cycle
212 comprised 2 h moisture generation (at a rate of 2.5 g/h) followed by 2 h of no moisture
213 generation (4 h total). The closed environment comprised a thermally and hygrically isolated
214 box (where $V = 1 \text{ m}^3$) with an air infiltration rate of 0.35 ACH h^{-1} . The initial indoor/ outdoor
215 air humidity ($\varphi_i = 0.5$, $\varphi_e = 0.5$ respectively) conditions were isothermal ($T_{\text{db}} = 23^\circ\text{C}$). The
216 fabric comprised 2 mm thick vapour barrier ($S_d = 1500 \text{ m}$) and 240 mm thick vacuum
217 insulation panel ($\lambda = 0.001$) (Fig. 2). A non-visualized internal component comprising 2 mm
218 thickness of mesoporous solid (area/volume ratio = 0.12 m^2) was used and the hygrothermal
219 functional properties taken from Table 1. The parameters for the numerical model were set to
220 have: (i) increased accuracy and adapted convergence, (ii) net volume = 1 m^3 , (iii) time step 1
221 min, (iv) optional climate (50% RH/ 23°C), (v) inner climate calculated, (vi) initial boundary
222 conditions (50% RH/ 23°C), (vii) 'fine' mesh grid spacing, and (viii) calculation accuracy of
223 $0.5\% / 0.5^\circ\text{C}$ for RH and T_{db} respectively.

224

225 2.3.3 Candidate isotherms

226 The first set of candidate isotherms were introduced ($A_1 - A_6$) and derived from MS 8.3, each
227 having identical moisture storage capacity (identical $\Delta w = 671 \text{ kg m}^{-3}$) within the specified
228 $\varphi_{i,L} - \varphi_{i,U}$ range, i.e. 0.45 - 0.55; 0.5 - 0.6; 0.55 - 0.65; 0.6 - 0.7; 0.65 - 0.75; 0.7 - 0.8 (Fig. 3a).
229 Fig. 3b shows the modal pore diameters derived from Kelvin's equation ranging from 2.85
230 nm to 6.56 nm, hypothetically created by altering pore wall thickness such that pore volume
231 remained unaltered (see Fig. 4b). The region of the isotherm between $\varphi_{i,L}$ (1st inflection point;
232 the onset of multilayer physisorption) and $\varphi_{i,U}$ (2nd inflection point; the percolation threshold)
233 corresponds to the available moisture storage capacity, Δw for RH buffering between upper/

234 lower limits (see Fig. 4a). A second set of isotherm candidates ($B_1 - B_4$) were introduced by
235 proportionally reducing the total pore volume (y-axis adjustment) from 90% to 60%. The A_3
236 candidate isotherm was used as a reference and so the modal pore diameter remained constant
237 (Fig. 5). The water absorption coefficient A derived from MS 8.3 was used for all candidates,
238 and the capillary transport coefficients (D_{ws} and D_{ww}) for use in the hygrothermal numerical
239 model were calculated after producing the water vapour isotherm [26].

240

241 2.3.4 Standardization and parametric studies

242 The next series of hygrothermal simulations aimed to determine the total permissible moisture
243 load (g/h) per unit mass (kg) before RH buffering failure occurred. Candidate isotherm A_3 ,
244 with an assumed area/volume ratio of 0.1200 (equivalent to 0.15 kg/m^3), was used as the
245 reference (based on the previous simulations) and parametrically assessed against a set of
246 eight new area/volume ratios: 0.0405, 0.0810, 0.1619, 0.2024, 0.2429, 0.2834, 0.3239, and
247 0.3643. This was done in order to set the standardization process of volumetric moisture loads
248 (ω_{ml}) in 1m^3 at $N = 60$. Same parameters for the hygrothermal numerical modelling were set
249 as described in Section 2.3.2. For ventilation sensitivity analysis, the simulations were
250 expanded at three different ACH (0.25, 0.5 and 0.7 h^{-1}). The effect of φ_e in diluting/
251 intensifying the interior moisture load was simulated. For this the simulations were expanded
252 by adding five new different φ_e values ($\varphi_e = 0.2, 0.3, 0.4, 0.6$ and 0.7). For both cases, the
253 internal moisture loads in the hygrothermal numerical modelling were added progressively
254 until material's failure was found; this set the curve of total moisture loads that a specific
255 quantity of material can cope. The accuracy of the curve was within 3%, so the error bars
256 would not be visible in some cases.

257

258 A representative selection of the ω_{ml} curves from previous parametric assessment (ACH =
259 0.25 h^{-1} and $\varphi = 0.5$; ACH = 0.7 h^{-1} and $\varphi = 0.5$; ACH = 0.35 h^{-1} and $\varphi = 0.2$; ACH = 0.35 h^{-1}
260 and $\varphi = 0.7$) were used in order to predict the total permissible moisture loads for the rest of

261 the isotherm candidates designed (A₁, A₂, A₄, A₅, A₆, B₁, B₂, B₃, and B₄). Expanded
262 hygrothermal simulations were done by selecting any x-axis and y-axis values (quantity of
263 material and ω_{ml} , respectively) from the predicted curves (see Section 3.3) and setting them
264 into the hygrothermal numerical modelling. The aim was to determine whether the fluctuation
265 of $\varphi(t)$, and the material's capacity for RH buffering within the specified operating limits (φ_{max}
266 = 0.70; φ_{min} = 0.55), could still be maintained.

267

268 2.3.5 Hygrothermal model validation

269 The water vapour isotherms for the two new materials were determined by gravimetric DVS.
270 A DVS Advantage-2 series (Surface Measurements Systems Ltd., London, UK) with
271 incorporated ultra-microbalance (1 μ g sensitivity) and fully automated weighing/ purging was
272 used to independently control T_{db} and RH to an accuracy of ± 0.5 K and $\pm 1.5\%$, respectively
273 (vapour pressure accuracy $\pm 1.5\%$ p/p₀). The data was recorded automatically in 1 min time-
274 steps using Advantage Control Software (ACS). Previous to the test and taring of the ultra-
275 microbalance, the chamber was left to fully equilibrate at 23 °C and at constant nitrogen flow
276 (10 sccm) for 1 h to ensure stability for baseline measurements accuracy. All samples were
277 outgassed under vacuum at 120 °C for 12 h. A pre-heating sequence was set in the ACS
278 (heating ramp rate of 2 °C/ min, from 23 °C) at 150 °C for 1 h prior to testing, to ensure that
279 $w = 0$. A counter weight in the reference pan was set to zero, and the dry samples (~ 0.02 g)
280 were loaded to set the initial mass. A full cycle of 21 steps (sorption/ desorption) was
281 programmed to increase with a targeted relative vapour pressure from $\varphi = 0.05$ to 1 ($\varphi = 0.05$
282 intervals) along with the change in mass step (0.001%/ min) until equilibrium moisture
283 content (EMC) was reached. This was performed at T_{db} 23 °C and to a constant water vapour
284 flow rate of 100 sccm (0.1 L/ min).

285

286 A set of three experiments of water vapour sorption/ desorption kinetics aimed to establish the
287 accuracy of the numerical model were undertaken using the DVS Advantage-2 series. The

288 kinetics of the moisture uptake was meant to sequentially fluctuate between pre-defined RH
289 limits (20 - 30%; 30 - 50%; and 50 - 70%). Each cycle comprised 2hrs of moisture sorption
290 (30 - 50% RH) followed by 2hrs of moisture desorption (50 - 30% RH) for a total period of
291 16 hrs (4 complete cycles). All samples were outgassed under vacuum at 120 °C for 12 h prior
292 to testing. The same pre-heating sequence was applied using ACS, as previously described.
293 Additionally, the samples were pre-conditioned within the DVS at constant mass to ensure
294 that w_{20} , w_{30} and w_{50} were at EMC before the cycles started. The same steps for taring and
295 equilibration of the chamber were done, and the samples (~ 0.02 g) were loaded to set the
296 initial mass. This was again performed at T_{db} 23 °C and to a constant water vapour flow rate
297 of 100 sccm (0.1 L/ min), as with previous experiments.

298

299 The hygrothermal numerical model setup was designed to sequentially perform the kinetics of
300 the moisture uptake between the pre-defined RH limits (20 - 30%; 30 - 50%; and 50 - 70%)
301 over a set number of cycles (as described previously – see Section 2.3.2 for description of the
302 closed environment and the parameters of the numerical model). Scaling of the volume from
303 the DVS chamber ($V_{ch} = 0.0002945 \text{ m}^3$) to the physical model ($V = 1 \text{ m}^3$) was done in order to
304 proportionally set the infiltration rate of 100 sccm ($0.006 \text{ m}^3 \text{ h}^{-1}$) and the material quantity
305 (0.02 g). As a result, a constant ACH = 20.37 h^{-1} and area/ volume ratio (0.01) of the non-
306 visualized component was estimated. The initial w was set according to each test (EMC at
307 w_{20} , w_{30} and w_{50}) intended to perform each sorption/ desorption cycle at constant temperature,
308 where $T_{db} = 23 \text{ °C}$.

309 **3. Results and discussion**

310 3.1. Sensitivity analysis of candidate isotherms

311 Fig. 6 shows the simulated RH buffering results for MS 3.3, 4.7 and 8.3 over the 4-hour cycle.
312 Repeated long-term loop cycling of the material resulted in progressive decay of their

313 capacity for humidity buffering in cases where the moisture load was always positive, i.e.
314 where no infiltration of lower moisture content air occurs. This decay caused the material to
315 fail after N number of cycles when the fluctuation of $\varphi(t)$ exceeded the $\varphi_{i,U}$ limit. There
316 appears to be no dependent correlation between N and modal pore diameter, where for MS
317 8.3, N = 6.5; MS 4.7, N = 3.5; and MS 3.3 N = 8.5. It was found that the number of decay
318 cycles, N, was highly sensitive to the value of Δw between $\varphi_{i,L}$ - $\varphi_{i,U}$ limits, i.e. controlled by φ
319 (x-axis) adjustments to the sorption isotherm and hence pore size distribution. From Fig. 7a it
320 appears that the largest proportion of water uptake (candidate isotherm A₃) corresponds to the
321 longest time for material failure. Furthermore, Fig. 7b shows a positive linear correlation
322 between the moisture storage capacity in the operating range of the isotherm ($\varphi_{i,L}$ - $\varphi_{i,U}$), in
323 this case Δw_{55-65} , and the time taken to exceed the $\varphi_{i,U}$ limit. Fig. 7b shows that this linear
324 correlation persists for B₁ - B₄, where reduction in pore volume gives a proportional increase
325 in elapsed time before buffering failure (or N cycles). The slope of $\Delta w/ t$ linear correlation
326 approximates that for other candidate isotherms that have been designed for different $\varphi_{i,U}$ and
327 $\varphi_{i,L}$ limits (Fig. 8a- c).

328

329 3.2. Closed environment parameters

330 Fig. 9a-b shows the simulated results where a non-linear positive correlation was found
331 between the interior moisture load per unit volume inside the closed environment, and the
332 minimum quantity (mass) of adsorbent required to achieve buffering between $\varphi_{i,L}$ and $\varphi_{i,U}$. As
333 the background air infiltration to the closed environment (ACH^{-1}) increased, the moisture
334 content of the infiltrating (exterior) air either adds to or subtracts from the interior moisture
335 load (g/s) and so the minimum mass of adsorbent required can be adjusted in accordance with
336 the trends shown in Fig. 9a-b. If $\varphi_{i,L} \leq \varphi_e \leq \varphi_{i,U}$, then the RH buffering capacity of the
337 adsorbent, and the surface area: volume ratio of adsorbent required becomes sensitive to ACH
338 ⁻¹. If $\varphi_e < \varphi_{i,L}$, the surface area: volume ratio of adsorbent reduces whilst N increases, and the

339 interior moisture loads can potentially be wholly offset by infiltration alone. Conversely, if φ_e
340 $> \varphi_{i,U}$, N decreases and the adsorbent may not be able to buffer the closed environment unless
341 ACH^{-1} is very low.

342

343 3.3. Moisture loads prediction

344 As the number of decay cycles N is highly sensitive to Δw , the permissible moisture loads
345 before failure (in this case at $N = 60$) could confidently be estimated for any candidate
346 isotherm and any closed environment scenario. Fig. 10 shows the dependency of Δw on the
347 added/ subtracted moisture load from infiltrating air (including infiltration rate) at different
348 outdoor air humidities, φ_e . Expanded numerical simulations showed good agreement where
349 the $\varphi_{i,L} - \varphi_{i,U}$ limits were not exceeded at $N = 60$. This hygrothermal numerical modelling
350 technique can therefore be applied to generate $\omega_{ml}/$ adsorbent mass graphs for any closed
351 environment scenario, from which the optimum surface area: volume ratio and air infiltration
352 rate can be selected.

353

354 3.4. Experimental work and model validation

355 Fig. 11 shows the water vapour isotherm (sorption/ desorption cycles) for the two new
356 materials (MCM-41₁₅₀/ MCM-41₁₈₀); both, having a distinctive Type V isotherm and type H2
357 hysteresis loop. From Fig. 11 it appears that there is a close fit between the ideal designed
358 isotherms (MS-5.38 and MS-8.24) and the experimentally achieved ones, indicating a good
359 correlation between their modal pore diameter and total pore volume. This was found to be
360 56% and 42% from the total pore volume (MS-5.38 and MS-8.24) for the cases of MCM-
361 41₁₅₀ and MCM-41₁₈₀, respectively. This indicates that for MCM-41₁₈₀ the difference in total
362 pore volume and modal pore diameter can be tuned by varying pore wall thickness during
363 (crystallisation) synthesis by controlled temperature variation.

364

365 The moisture content between $\varphi = 0.65$ and 0.80 was found to be $\Delta w_{65-80} = 407.5 \text{ kg m}^{-3}$ for
366 MCM-41₁₅₀, $\Delta w_{65-80} = 256.4 \text{ kg m}^{-3}$ for MCM-41₁₈₀. Whereas between $\varphi = 0.70$ and 0.85 , this
367 was found to be $\Delta w_{70-85} = 267.7 \text{ kg m}^{-3}$ and 307.0 kg m^{-3} , respectively. The numerical
368 simulations showed that the resultant progressive decay of their capacity was highly sensitive
369 according to their highest Δw values. Evidence of this is shown in Fig. 12 for the RH
370 buffering results where the number of decay cycles, N was ~ 1.7 times higher for MCM-41₁₅₀
371 compared to MCM-41₁₈₀. Here, the onset of multilayer physisorption (i.e. steep slope of Δw
372 gradient at $\varphi = 0.65$ - arrow seen in Fig. 11) is clearly higher for the MCM-41₁₅₀. This resulted
373 in lowering the fluctuation of $\varphi(t)$ below the $\varphi_{i,U}$ limit. Conversely, Fig. 13 shows a significant
374 increase in the number of decay cycles ($N = 12$) for MCM-41₁₈₀, which corresponds to a
375 higher $\Delta w_{70-85} = 39.3 \text{ kg m}^{-3}$ compared with MCM-41₁₅₀.

376

377 Fig. 14 shows the comparison between the experimental DVS and numerical simulations
378 results for the three water vapour sorption/ desorption kinetics experiments (A, B and C).
379 Experimentally, EMC was achieved within $N = 4$ with a distinctive steep sorption/ desorption
380 gradient (suggesting rapid response for moisture sorption/ desorption) for all cases except
381 MCM-41₁₅₀ operating at 50 - 70% RH. This could partially be an indication of pronounced
382 scanning curves within this region of the H2 hysteresis loop, and partially as a result of
383 having a higher Δw gradient ($\Delta w_{50-70} = 179.5 \text{ Kg m}^{-3}$) compared with MCM-41₁₈₀ (see Fig. 11
384 and Fig. 14c). With the exception of MCM-41₁₈₀, operating in the 20 - 30% and 30 - 50% RH
385 ranges (full sorption/ desorption reversibility), it was found that the numerical predictions for
386 both the moisture uptake capacity and the rate of sorption (kinetics) were typically
387 underestimated. This could be attributable to the current absence of hysteresis loop and
388 associated scanning curve predictions within state-of-the-art hygrothermal simulation
389 techniques, and so clearly highlights this as a priority for future research.

390

391 4. Conclusions

392 A top-down predictive design tool that enables the design of an ideal water vapour sorption
393 isotherm for any RH buffering application was developed and experimentally tested. The
394 simulated results of this technique probed MCM-41 type materials and found that they can
395 provide a wide range of suitable candidates for synthesizing/ modulating mesopore geometry
396 and to enable optimisation of hygrothermal functional properties with respect to RH
397 buffering. Evidence of this was found in the close fitting between experimental and designed
398 isotherms and within a range that can be accurately matched or predicted by the design tool.
399 Consistent agreement was found when correlating pore volume with pore wall thickness
400 variance from the synthesis process, indicating a positive correlation between their Δw and the
401 time in time in exceeding $\varphi_{i,U}$.

402

403 The simulated results showed that for any RH buffering application, the progressive decay for
404 humidity buffering was independent of modal pore diameter and had a positive correlation
405 with Δw between the $\varphi_{i,L}$ - $\varphi_{i,U}$ limits. Evidence of this was found in a positive linear trend
406 between Δw and the time taken to exceed $\varphi_{i,U}$. This suggested that when designing an ideal
407 isotherm for a specific application, adjustment of the maximum Δw should be allocated
408 between the operating limits $\varphi_{i,L}$ - $\varphi_{i,U}$. A methodological illustration of the refinement
409 technique logic for the design process of an ideal isotherm is presented in Fig. 15; a brief
410 summary of steps (a) to (f) referred to it are as follows:

- 411 a) Preliminary assessment using the hygrothermal numerical model for any MS material
412 (light blue line) under a specific buffering application, where fluctuation of $\varphi(t)$ is
413 analysed within/ outside the $\varphi_{i,U}$ and $\varphi_{i,L}$ limits
- 414 b) Design a set of isotherm candidates from the MS material (light blue line), using its
415 maximum w to set the maximum theoretical n possible
- 416 c) Corresponding PSD histogram derived from the isotherm candidates in (b)

- 417 d) Sensitivity analysis for all new candidates in (b) using the hygrothermal numerical
418 model from (a). The aim is to find the most suitable water isotherm for the application
419 e) The ideal water isotherm is found (pink line) at a corresponding gradient between I_L
420 and I_U , which steadily allowed for hygrothermal buffering at a higher number N of
421 cycles from (d)
422 f) Further adjustment of the water isotherm related to φ (x-axis) and w (y-axis)
423 adjustments, results in a variety of modal pore diameter and pore volume respectively
424 for any kind of buffering applications

425

426 Expanded numerical simulations showed that for a closed environment, a positive non-linear
427 correlation between the total permissible ω_{ml} and the mass of adsorbent required to fully
428 achieve buffering between $\varphi_{i,L}$ and $\varphi_{i,U}$ was established. It was found that the RH buffering
429 capacity and the volume ratio of the adsorbent were controlled by φ_e and ACH^{-1} ;
430 undermining/ improving the material's failure at N cycles. Furthermore, the permissible ω_{ml}
431 changes proportionally with Δw from an ideal isotherm, and therefore could confidently be
432 estimated for any candidate isotherm and any closed environment scenario. On the other hand,
433 it was evident from the experimental results that the kinetics of the dynamic behaviour of
434 water vapour sorption/ desorption (possible presence of scanning curves development within a
435 specific hysteresis loop) is still not fully implemented by current hygrothermal numerical
436 models. However, in this study some exceptions were found (MCM-41₁₈₀ at the 20 - 30% and
437 30 - 50% RH limits), from which the concept of full sorption/ desorption reversibility enables
438 hygrothermal structure-properties assessment.

439

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445 WS.

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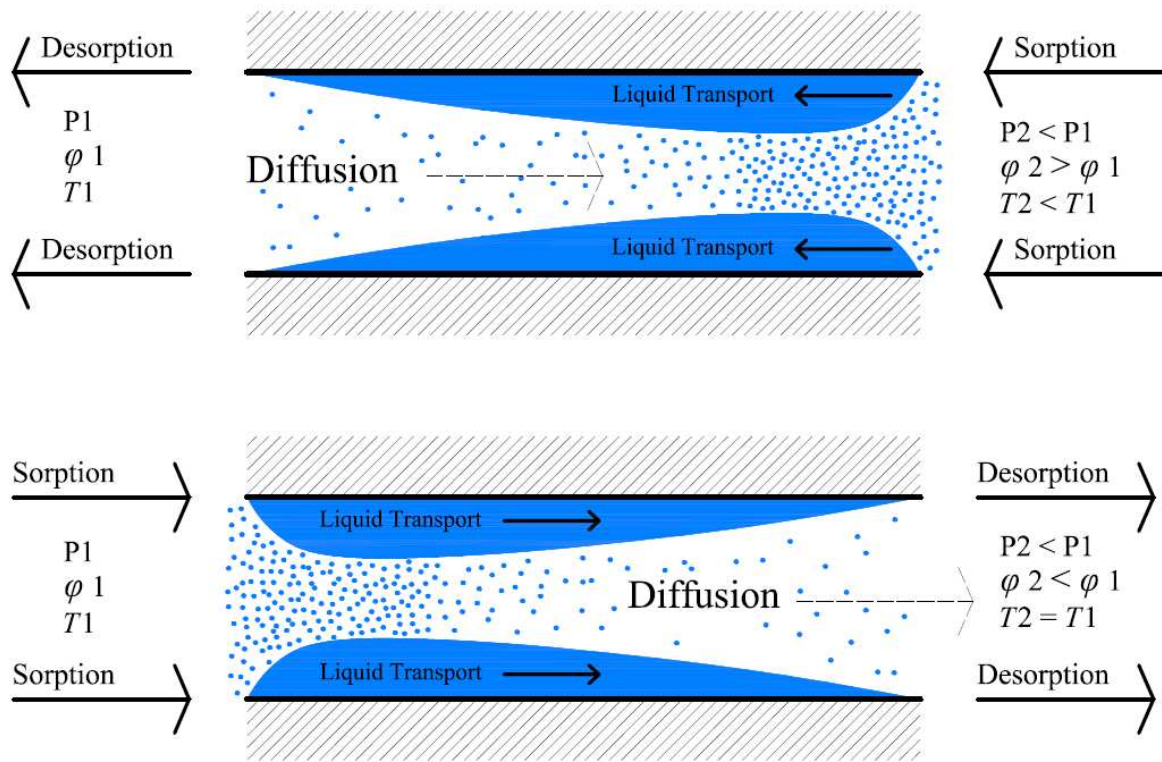
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530

531 7. List of figures

532



P = Water vapour partial pressure, φ = Relative humidity and T = Dry bulb air temperature

Figure 1 – Contra - and counter flow of mass transport. Adapted from [27]

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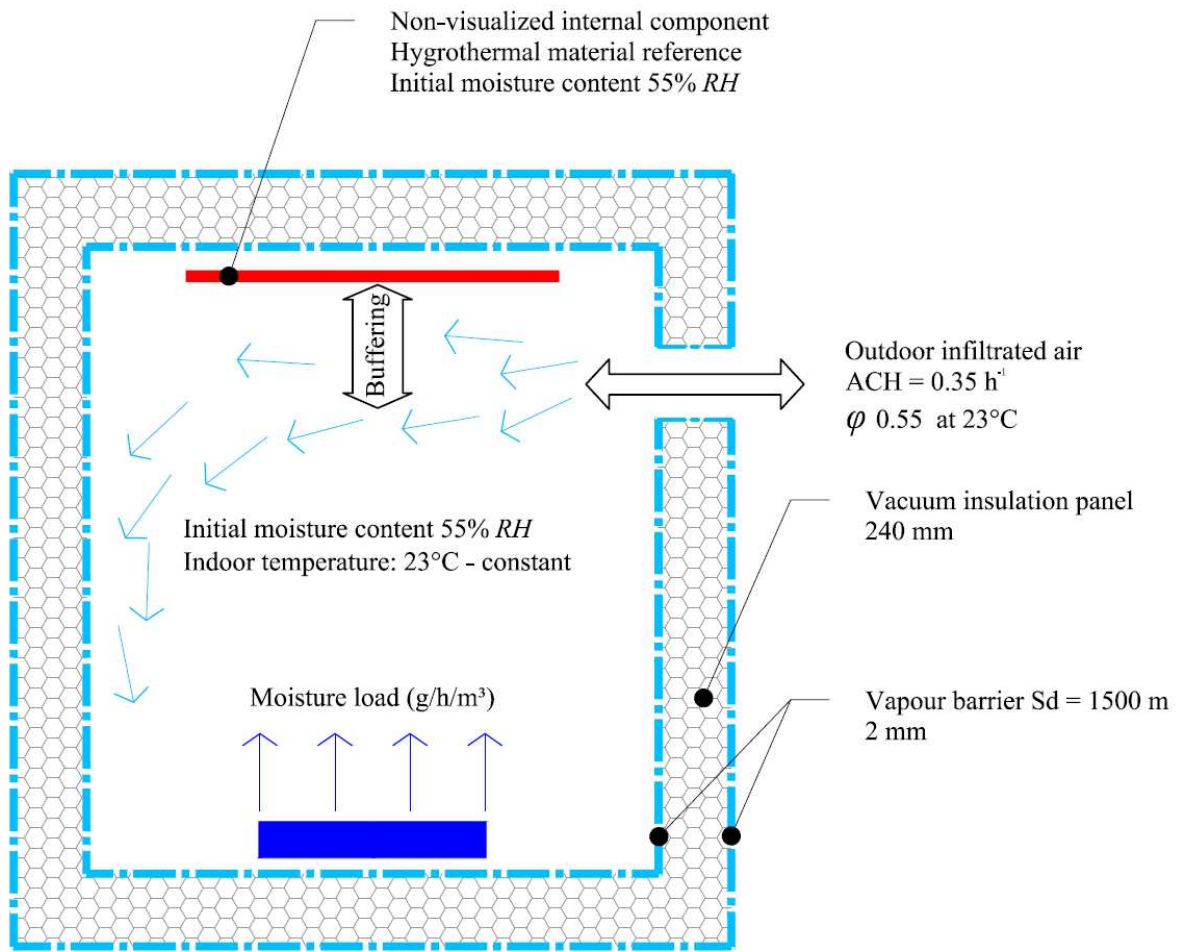


Figure 2 – Closed environment scheme

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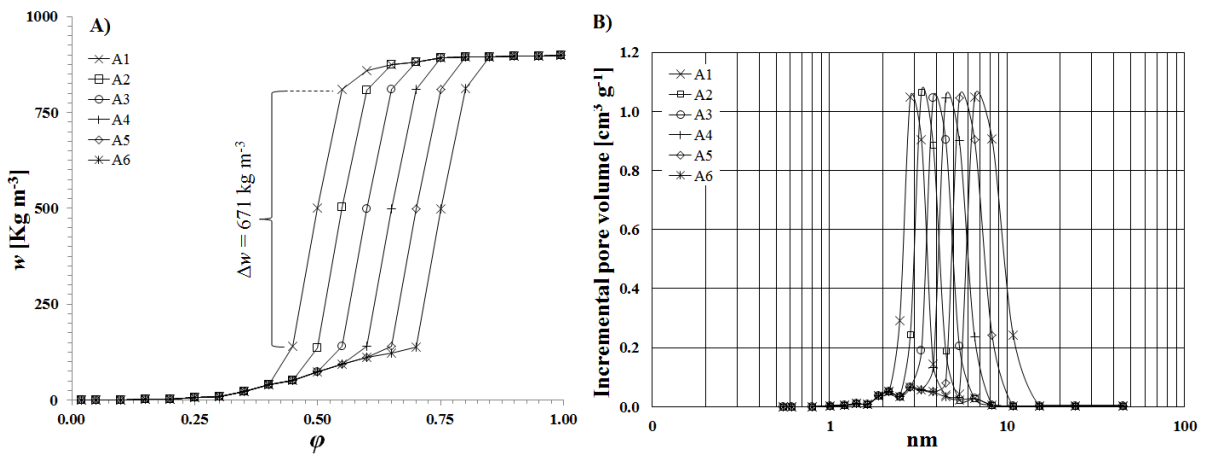


Figure 3 – Hypothetical water vapour isotherm, a) available moisture capacity Δw , b) constant modal pore diameter and n

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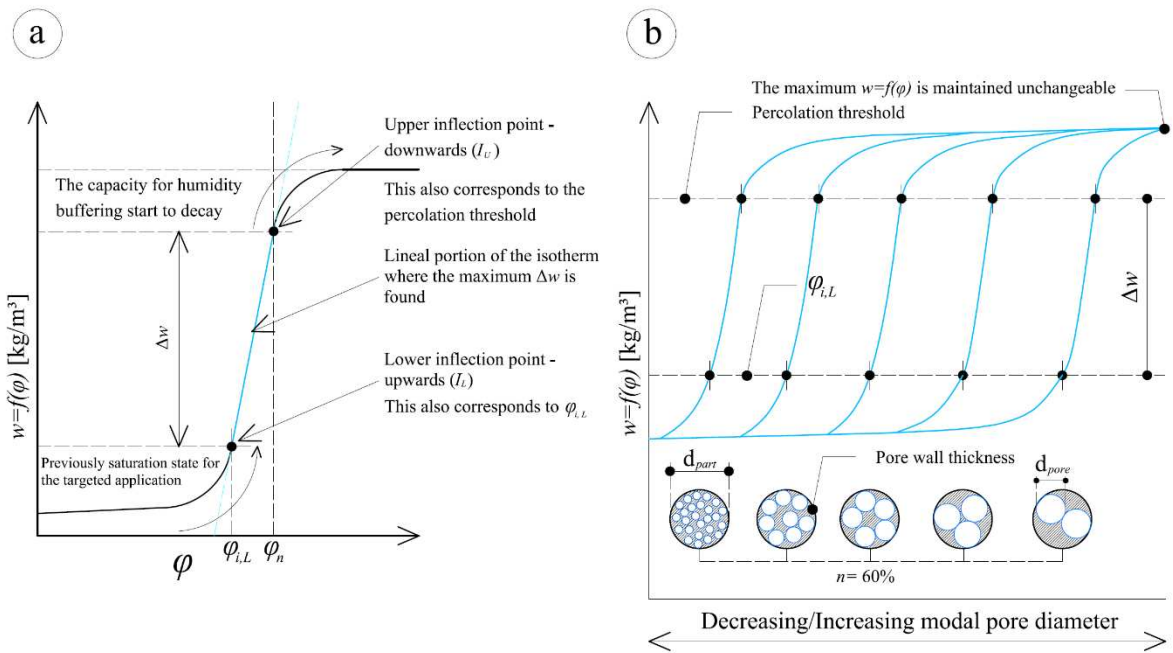


Figure 4 – RH buffering results for MS-3.3, 4.7 and 8.3

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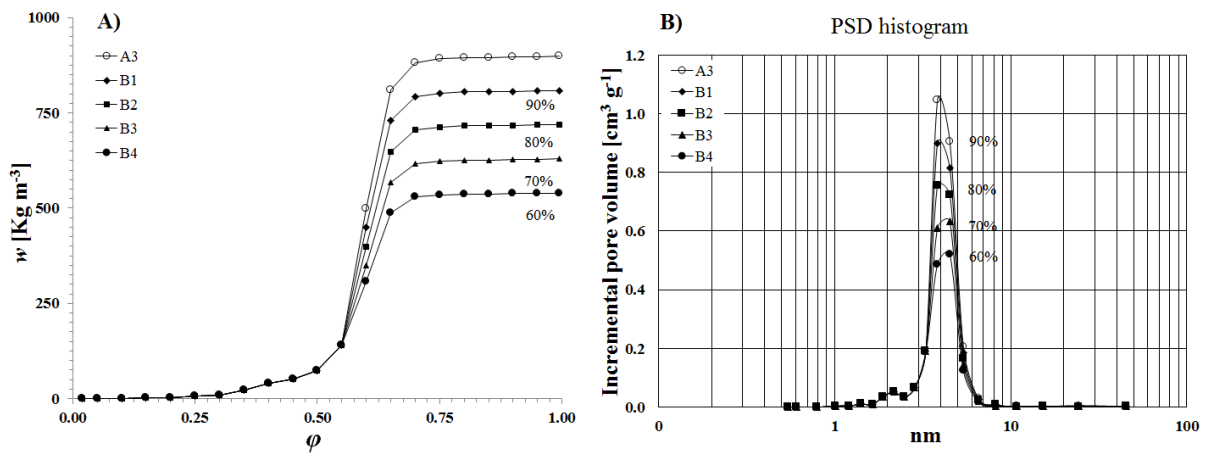


Figure 5 – Isotherm candidates, a) sorption isotherms, b) modal pore diameter derived from Kelvin's equation

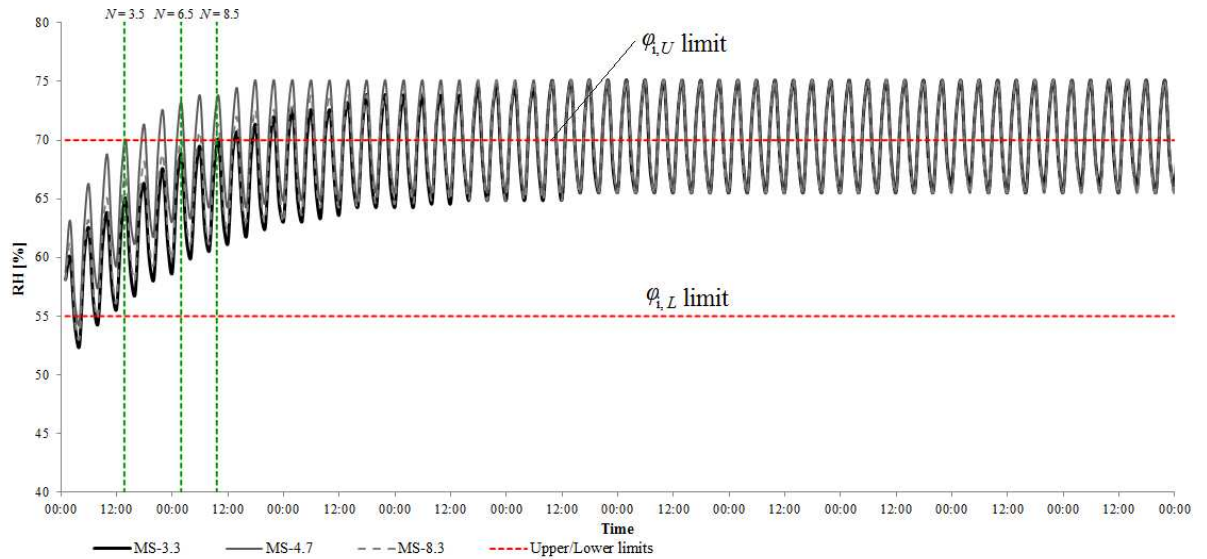


Figure 6 – Correlation between Δw and moisture storage decay, a) water uptake at Δw range, b) $\Delta w/ t$ linear correlation

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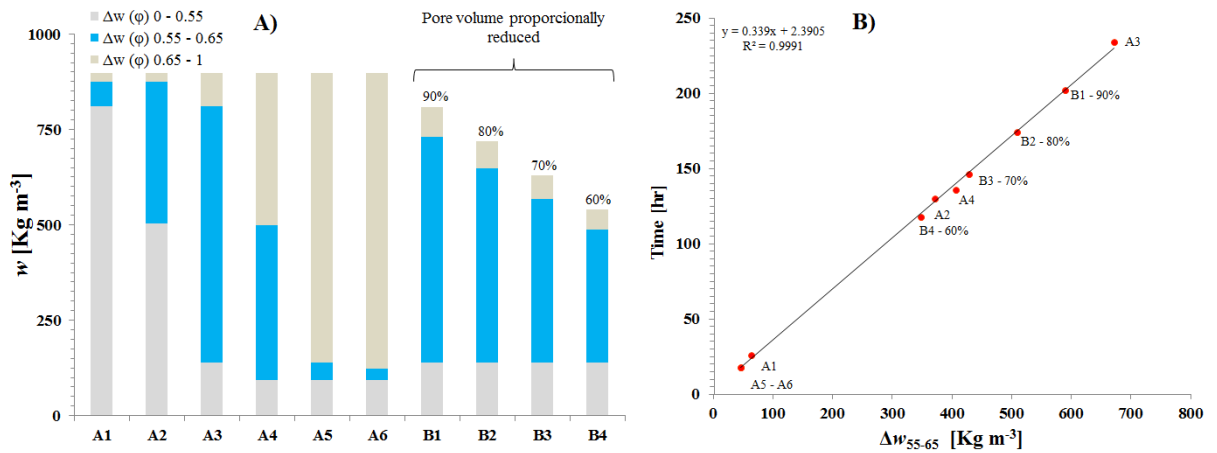


Figure 7 – Isotherm candidates – total pore volume proportionally reduced, a) sorption isotherms, b) modal pore diameter derived from Kelvin's equation

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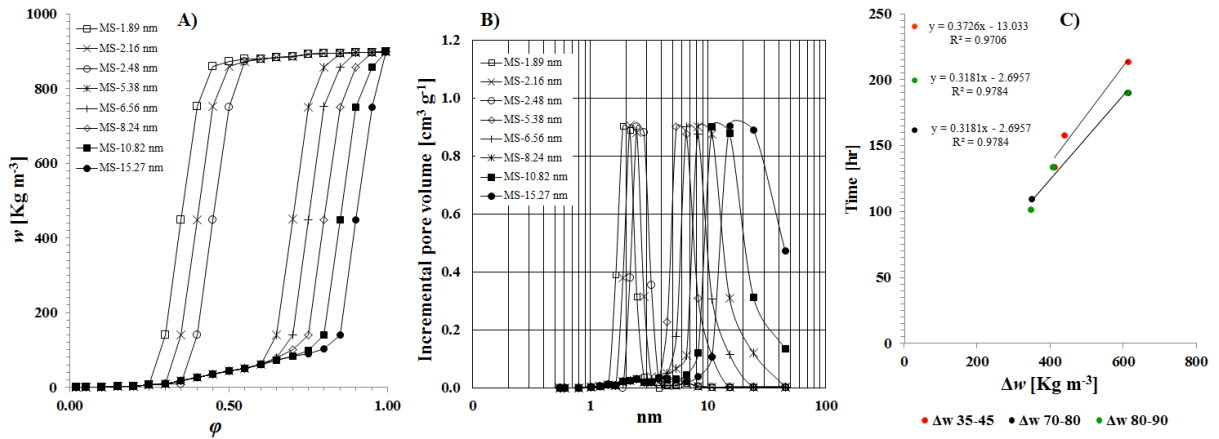


Figure 8 – Isotherm candidates for different $\phi_{i,U}$ and $\phi_{i,L}$ limits, a) sorption isotherms, b) modal pore diameter derived from Kelvin's equation, c) $\Delta w / t$ linear correlation

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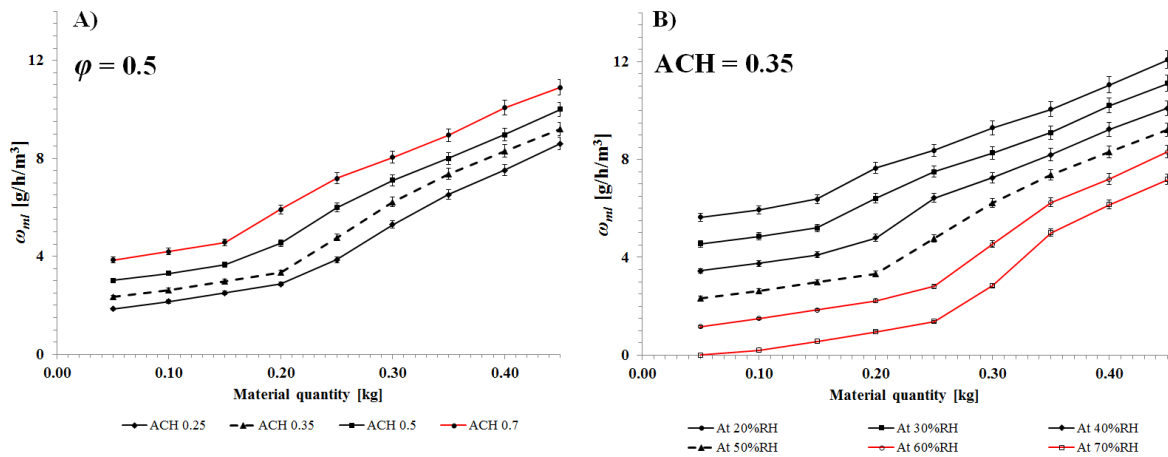


Figure 9 – Permissible volumetric moisture load curves, a) constant RH, b) varying ACH

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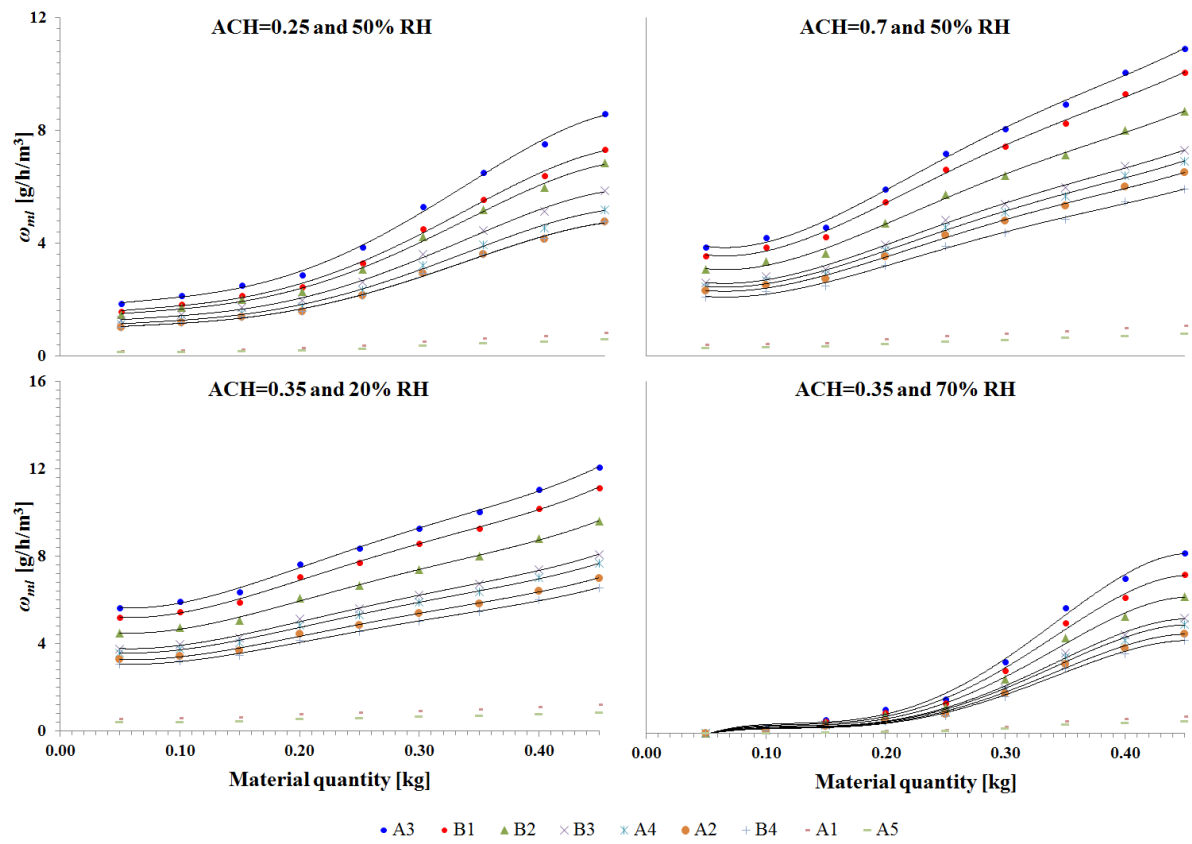


Figure 10 – Prediction of volumetric moisture load curves for designed isotherm candidates

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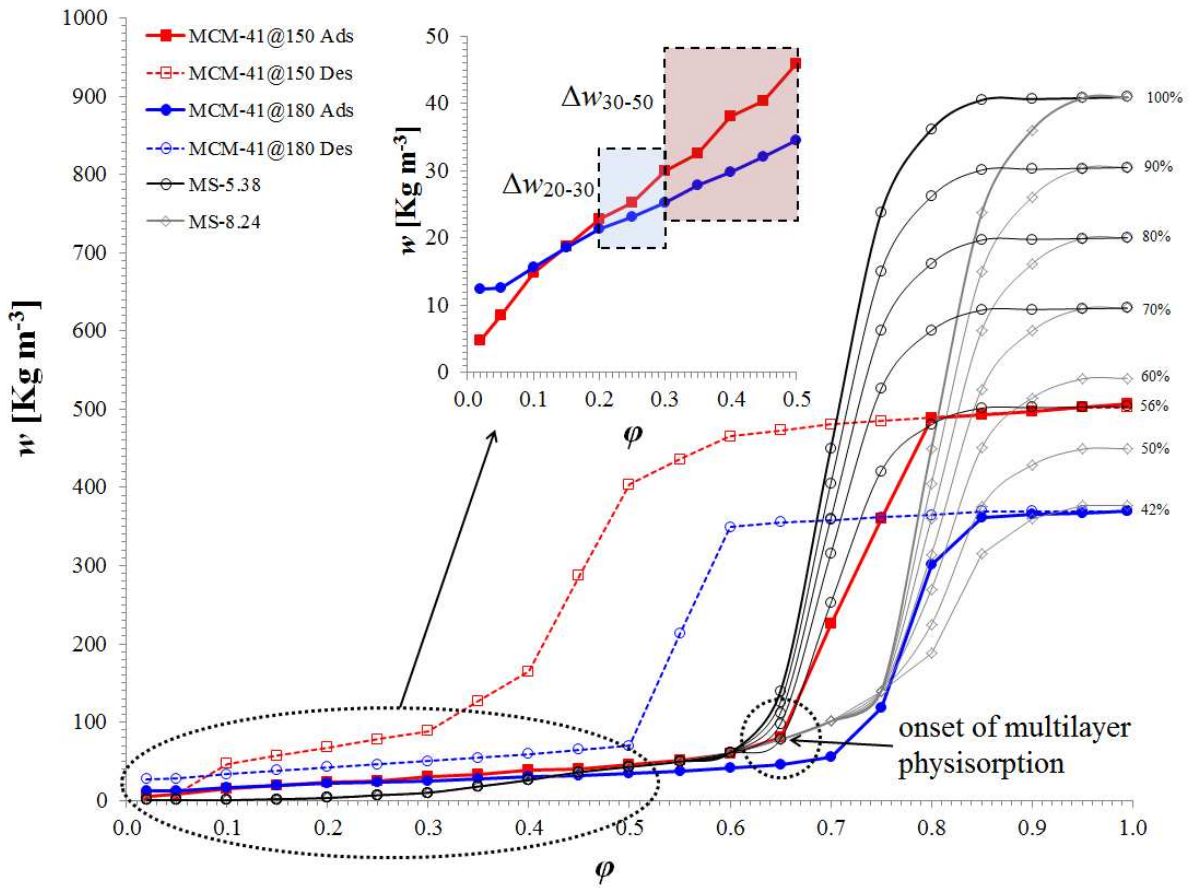


Figure 11 – Designed and experimental water vapour isotherms

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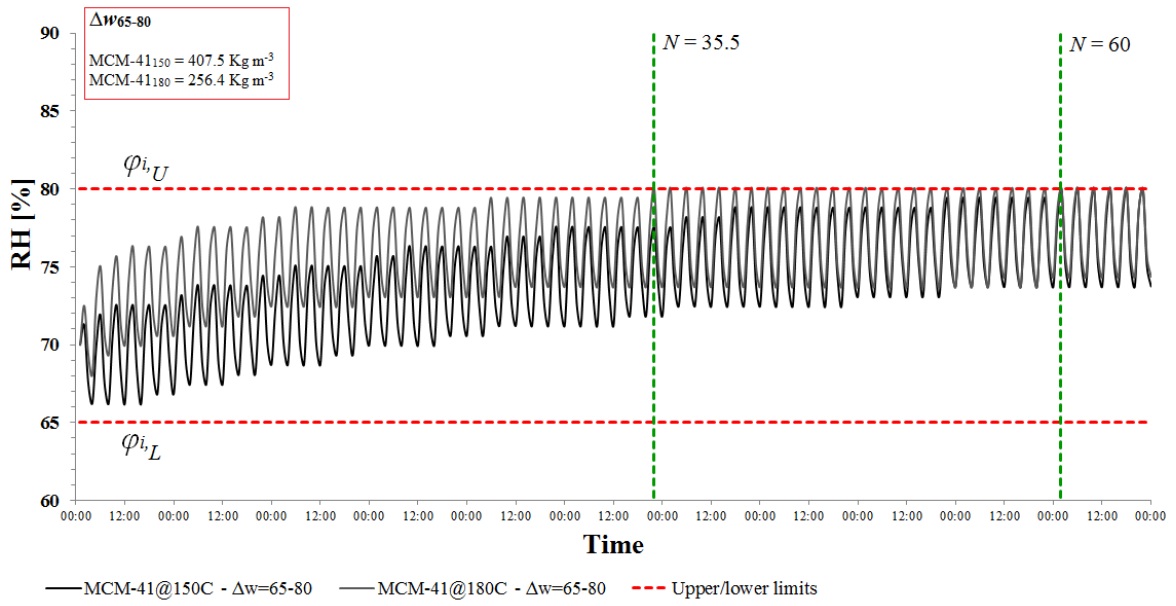


Figure 12 – RH buffering results for MCM-41₁₅₀ and MCM-41₁₈₀ – buffering application between $\varphi_{i,U} = 0.8$ and $\varphi_{i,L} = 0.65$

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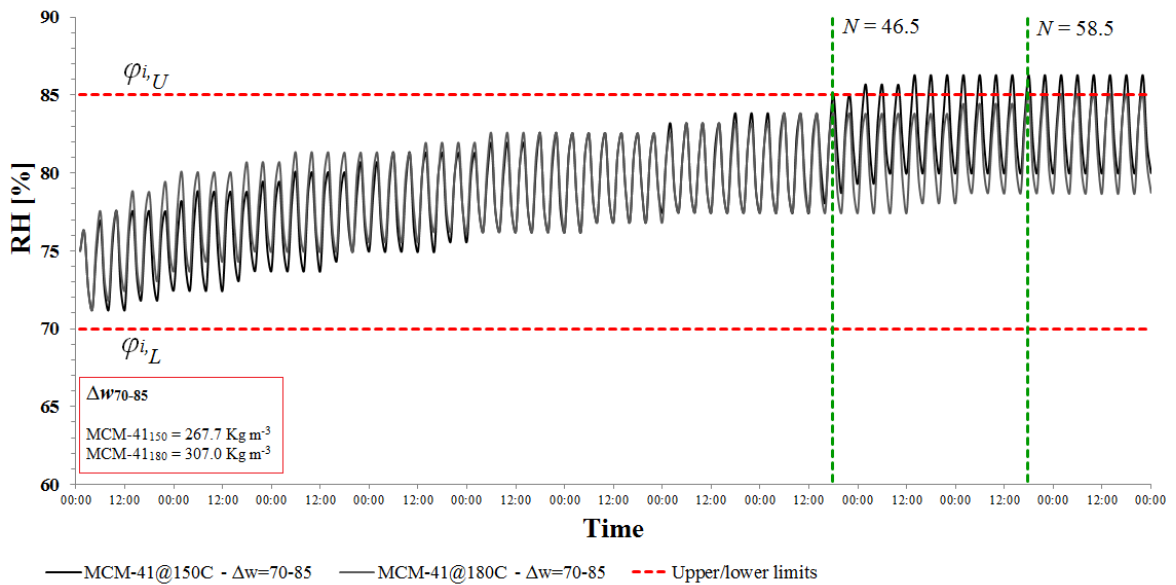


Figure 13 – RH buffering results for MCM-41₁₅₀ and MCM-41₁₈₀ – buffering application between $\varphi_{i,U} = 0.85$ and $\varphi_{i,L} = 0.7$

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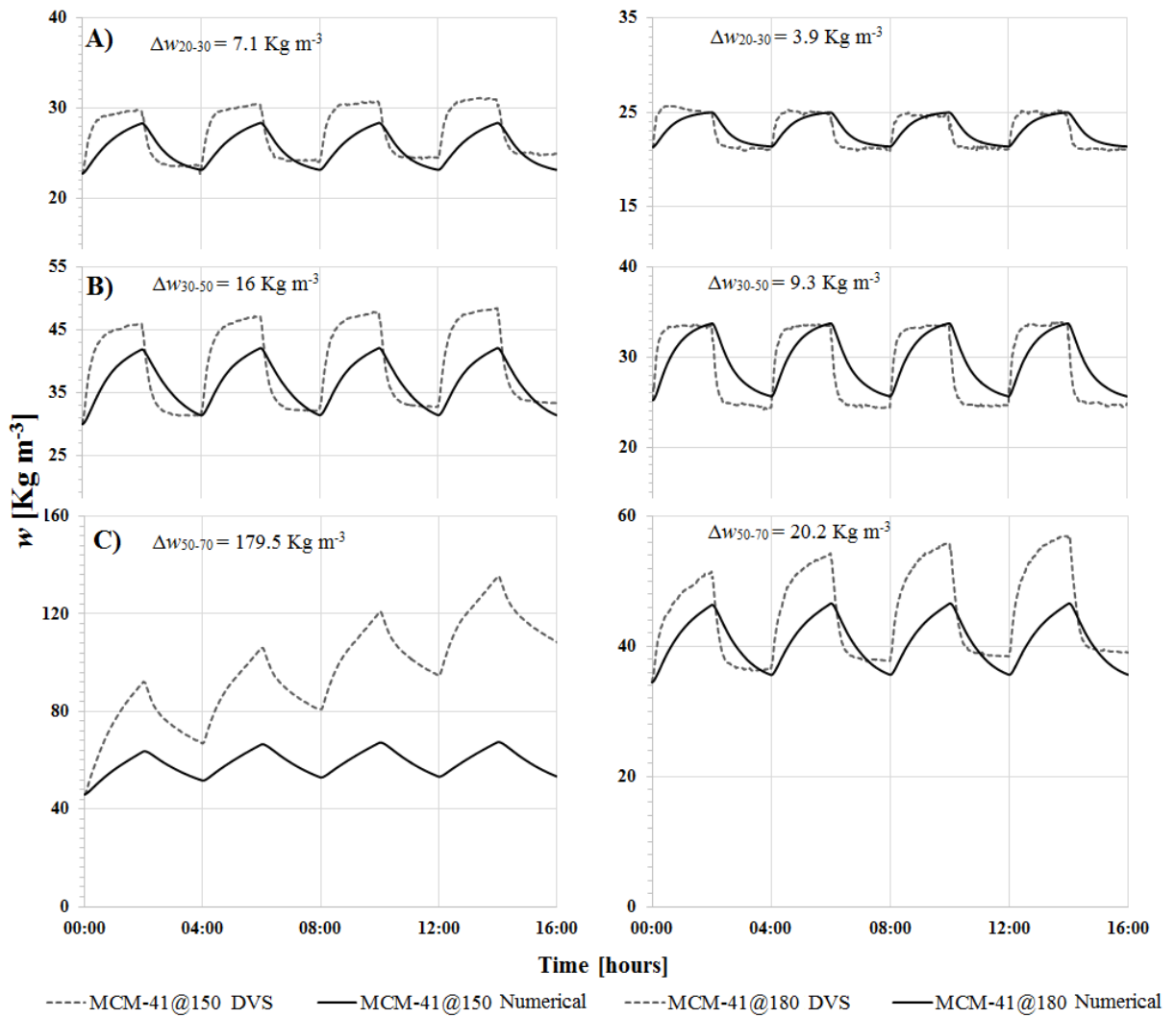


Figure 14 – Vapour sorption/ desorption kinetics in pre-defined RH limits, a) 20 - 30%, b) 30 - 50%, and c) 50 -70% – Comparison between numerical and experimental data

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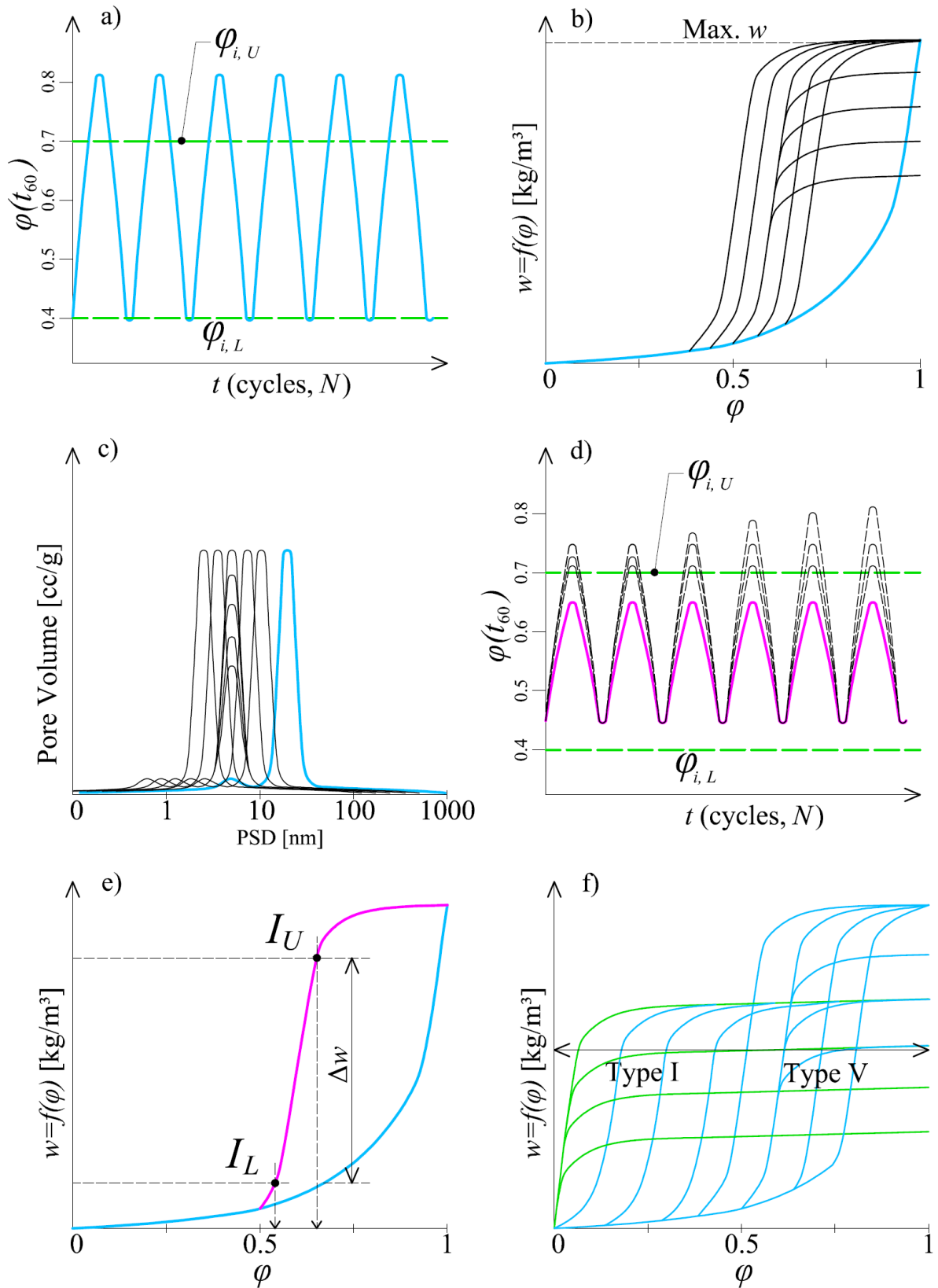


Figure 15 – Methodological illustration for the design process of an ideal isotherm

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601 **8. Tables**

| Material | \varnothing_{pore} | ρ_{dry} | n | c_p | λ | w_{20} | w_{50} | w_{80} | w_f | A | μ |
|---------------------|----------------------|-------------------|--------------------------------|--------|-----------|-------------------|----------|----------|-------|------------------------------------|-------|
| | nm | kg/m ³ | m ³ /m ³ | J/kg·K | W/m·K | kg/m ³ | | | | kg/m ² s ^{0.5} | --- |
| MS 3.3 ^A | 3.3 | 501 | 0.76 | 1011 | 0.05 | 12 | 79 | 247 | 346 | 2.112 | 4.54 |
| MS 4.7 ^A | 4.7 | 336 | 0.85 | 1866 | 0.05 | 8 | 33 | 105 | 363 | 0.561 | 7.13 |
| MS 8.3 ^A | 8.3 | 618 | 0.76 | 1691 | 0.05 | 5 | 86 | 295 | 865 | 0.550 | 10.52 |

Table 1 – Hygrothermal functional properties for mesoporous silicas – ^A Values taken from reference [20, 43]

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