



HAL
open science

Experimental investigation of the effect of temperature on the first desorption isotherm of concrete

Stéphane Poyet

► **To cite this version:**

Stéphane Poyet. Experimental investigation of the effect of temperature on the first desorption isotherm of concrete. *Cement and Concrete Research*, 2009, 39 (11), pp.1052-1059. 10.1016/j.cemconres.2009.06.019 . cea-01272821v1

HAL Id: cea-01272821

<https://cea.hal.science/cea-01272821v1>

Submitted on 11 Feb 2016 (v1), last revised 21 Jul 2021 (v2)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Experimental investigation of the effect of temperature** 2 **on the first desorption isotherm of concrete**

3 Stéphane POYET

4 CEA Saclay, DEN/DANS/DPC/SCCME/LECBA, B158, 91191 Gif sur Yvette Cedex, France

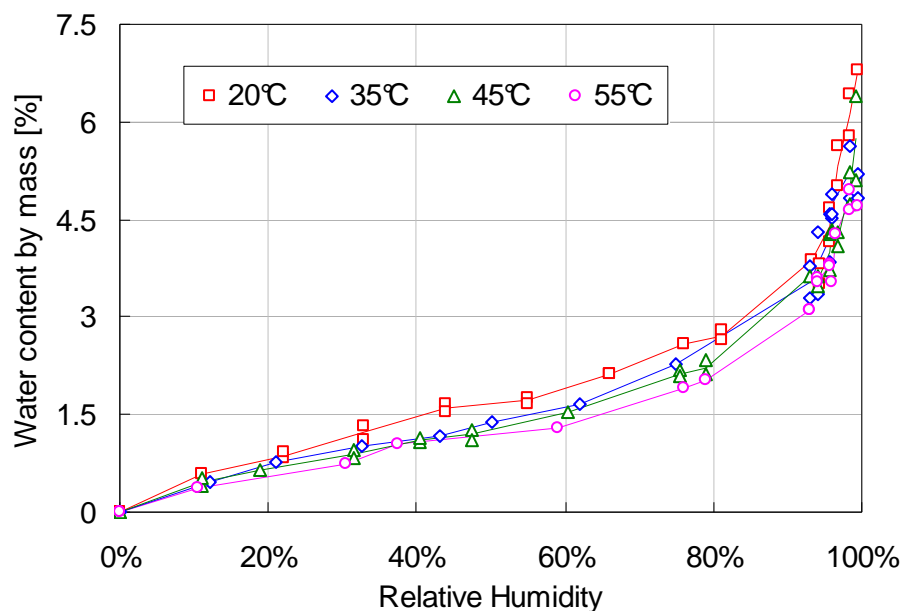
5 **1. Abstract**

6 In the framework of the radioactive waste management in France, interim storage concrete
7 structures should be submitted to temperature up to 80°C and subsequent desiccation. The
8 impact of temperature on the sorption properties of concretes has been poorly studied and
9 results are scarce. An experimental campaign was thus carried out to characterize the first
10 desorption isotherms of a modern concrete at 30°C and 80°C. The results show a significant
11 influence of the temperature increase that will have to be accounted for the durability
12 assessment of the long-term interim storage concrete structures. Investigating the causes of
13 these modifications, it appeared that desorption induced by temperature might be the
14 principal mechanism rather than microstructure alteration and water properties evolution.

15 **2. Introduction**

16 In the framework of radioactive waste management, the concrete structures for radioactive
17 waste management are expected to undergo significant heating due to the waste thermal
18 power. In the French concept of subsurface structures, the cooling is likely to be achieved
19 using natural convection with air taken from outside. Doing so, the concrete temperature is
20 expected to reach (but not to exceed) 80°C in normal conditions and the concrete structure is
21 expected to undergo severe drying (due to the temperature increase of the ambient air) [1;
22 2]. The durability assessment of these structures over 300 years thus requires the accurate
23 knowledge of the sorption properties of concretes at such unusual temperature levels with
24 particular interest in desorption (corresponding to the drying process).

25 The influence of temperature on the sorption isotherms has been poorly studied and
26 experimental results are scarce in the scientific literature. Among these studies Daian has
27 experimentally determined the adsorption isotherms of a water-cured mortar at four different
28 temperatures: 20, 35, 45 and 55°C [3; 4]. The samples have been initially dried at 80°C and
29 then exposed to different increasing RH for the four temperatures. The curves thus obtained
30 are reproduced on Fig. 1 (according to the results published in [4]). The temperature
31 influence can be summarised as follows: the higher the temperature, the less the amount of
32 water adsorbed. Nevertheless, the offset between the curves obtained at 20°C and 55°C was
33 found to be low.



34

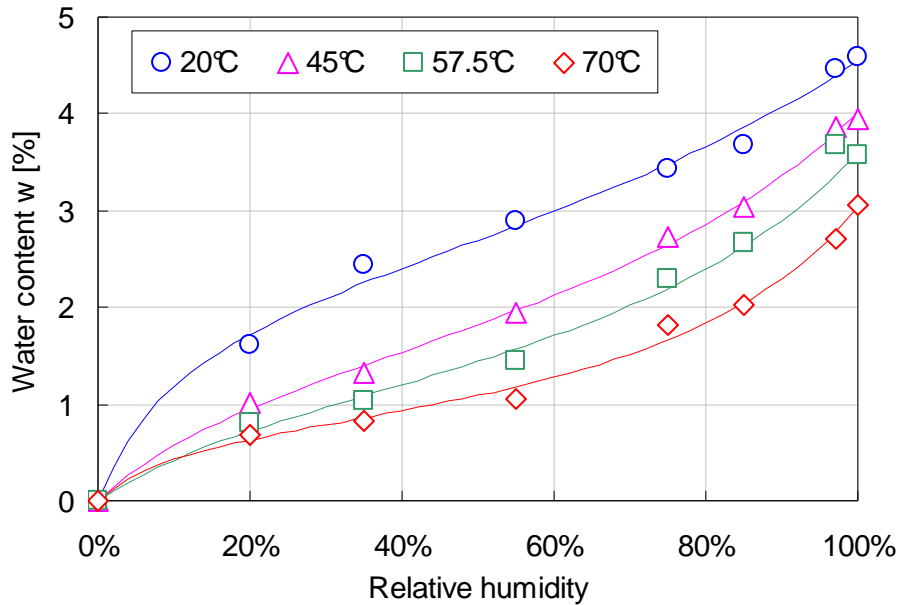
35 Fig. 1. Adsorption curves for a mortar between 20°C and 55°C after Daian [4].

36 This observation is in good agreement with the experiments of Radjy et al. [5] who
37 characterised the first adsorption branch of two mature (about two years old) steam-cured at
38 early-age (at nearly 100°C) hardened cement pastes with water-to-cement ratio (W/C ratio)
39 equal to 0.35 and 0.45 respectively for temperatures between 0°C and 60°C. The results
40 have shown a very limited dependence of the isotherms to temperature in this range. In the
41 same way, the first desorption isotherm of a mature (kept one year under water) hardened
42 cement paste cured at ambient temperature with a W/C ratio equal to 0.50 was characterised

43 for temperatures between 0°C and 40°C. As mentioned before, the resulting desorption
44 isotherms showed hardly any dependence on the temperature used.

45 In a recent attempt to develop a model capable of predicting the behaviour of concrete in any
46 arbitrary environment Ishida et al. [6] have characterised the sorption isotherms (the first
47 adsorption and the first desorption branches) of an 80-day water-cured hardened cement
48 paste (W/C ratio equal to 0.50) for 20°C, 40°C and 60°C. The results obtained for the first
49 adsorption have shown little differences between the curves for the three temperatures.
50 However, the results of the first desorption appeared to be much different: the first desorption
51 isotherm was greatly modified by the temperature increase. The decrease of the amount of
52 water adsorbed at higher temperatures was more pronounced than that obtained for
53 adsorption. Moreover the shape of the isotherms was also modified by the temperature
54 increase.

55 These facts have already been pointed at by Hundt & Kantelberg [7] who characterised the
56 first desorption isotherm of different cementitious materials for temperatures ranging from
57 20°C to 70°C. The results obtained with a 3.6 year old mortar (W/C ratio equal to 0.50) are
58 reproduced on Fig. 2 (according to the data published in [7]). As mentioned before the higher
59 the temperature, the less the amount of water adsorbed at equilibrium. One can see on Fig.
60 2 that the 20°C desorption isotherm was nearly a straight line. This pattern was greatly
61 modified when working at higher temperatures: see for instance the linear part between 20%
62 and 50% with a decreasing slope related to the temperature increase and the pronounced
63 upwards deviation for high RH. In addition, one can note the significant decrease of the
64 amount of water adsorbed at saturation as a function of temperature: the higher the
65 temperature, the lesser the amount of water at saturation. Hardened cement pastes with
66 varying W/C (between 0.40 and 0.55) and concretes with various preliminary treatments
67 were also tested by Hundt & Kantelberg [7], all the results obtained in this study (various
68 cementitious materials with various curing methods) confirm all these observations.



69

70 Fig. 2. First desorption isotherms for a mature mortar for four temperatures ranging from
 71 20°C to 70°C according to Hundt & Kantelberg [7].

72 An experimental campaign was then undertaken to highlight the influence of temperature and
 73 gather experimental data for further numerical approaches and durability assessment of
 74 interim storage concrete structures. The first desorption isotherm of a modern high-
 75 performance concrete was characterised at 30°C and 80°C. The temperature dependence of
 76 cementitious materials sorption properties is generally related to the coarsening of the pore
 77 structure (ettringite dissolution and C-S-H alteration) together with the evolution of water
 78 properties [8-11]. In this study, the examination of the results obtained indicates that another
 79 phenomenon may be at work and suggests that the microstructure alteration and the water
 80 properties evolution may have negligible effects.

81 **3. Experimental programme**

82 **3.1. Material tested**

83 The material used for the experiments was a modern high-performance concrete, the
 84 formulation is reported on Tab. 1. It is based on CEM I cement. The water-to-cement ratio
 85 (by weight) is equal to 0.43. This formulation was used because it is one of those which are

86 studied in the framework of radioactive waste management by the French agency for
 87 radioactive waste management (Andra).

88 Tab. 1. Concrete formulation

Component	Nature	Origin	Qty	Unit
Cement	CEM I 52.5	Lafarge Val d'Azergues, France	400	kg/m ³
Sand	Calcareous [0-5]	Boulonnais quarry, France	858	kg/m ³
Gravel	Calcareous [5-12.5]	Boulonnais quarry, France	945	kg/m ³
Water	-	-	172	L/m ³
Superplasticizer	Glenium 27	BASF	10	kg/m ³

89 The main properties of the concrete have been determined experimentally on samples taken
 90 out of the same batch and cured more than one year under water at 20°C. The values
 91 obtained are reported on Tab. 2. All the characterization tests were performed on saturated
 92 samples at 20°C (except for the gas permeability measurements and water porosity which
 93 implied complete drying at 60°C) and after thermal treatment at 80°C (until constant mass
 94 was achieved, residual properties after cooling). The intrinsic permeability to gas (nitrogen)
 95 was estimated using the Klinkenberg approach [12].

96 Tab. 2. Main concrete properties, all given data are at least the mean of three values

Concrete properties	20°C	80°C	Unit
Tensile splitting strength (Brazilian test)	5.80	4.95	MPa
Compressive strength	89.7	79.5	MPa
Elastic modulus	49.2	41.7	GPa
Poisson's ratio	0.18	0.17	-
Water porosity	11.3	12.0	%
Intrinsic permeability (nitrogen)	$2.0 \cdot 10^{-17}$	$4.2 \cdot 10^{-17}$	m ²
Klinkenberg coefficient	0.13	0.06	MPa
Heat conductivity	2.49	2.09	W/mK

97 The porosity to water at 30°C and 80°C was estimated using the mass loss obtained using
 98 silica gel (RH~3%). It was also estimated using two other usual experimental protocols:
 99 drying at 60°C with silica gel and drying at 105°C. All the results are presented in Tab. 3. The
 100 concrete saturated density was calculated using hydrostatic weighing, the mean value was
 101 found to be equal to 2.48.

102 Tab. 3. Porosity to water according to the experimental protocol.

Protocol	30°C (silica gel)	60°C (silica gel)	80°C (silica gel)	105°C (no silica gel)
Porosity to water	10.7%	11.3%	12.0%	12.3%

103 **3.2. Technique used**

104 The concrete first desorption isotherm was determined at 30°C and 80°C. The desiccator
105 method using saturated salt solutions was chosen for its simplicity and its reliability. This is a
106 standalone system which minimises human interventions and is recommended by the
107 European Committee for Standardization [13]. The different RHs which were used are given
108 in Tab. 4. For RH=100% deionised water was used (without any salt) and for RH=3% silica
109 gel was used (without water). The saturated salt solutions were prepared according to
110 international recommendations [13; 14] and the resulting RHs were verified before use.

111 Tab. 4. RH investigated and corresponding saturated salt solutions.

Salt used	Formula	RH obtained at	
		30°C	80°C
Deionised water	H ₂ O	100%	100%
Potassium sulphate	K ₂ SO ₄	96%	95%
Sodium sulphate	Na ₂ SO ₄ 10 H ₂ O	-	90%
Potassium nitrate	KNO ₃	90%	-
Potassium chloride	KCl	85%	-
Sodium chloride	NaCl	75%	74%
Sodium nitrate	NaNO ₃	-	65%
Ammonium nitrate	NH ₄ NO ₃	63%	-
Sodium bromide	NaBr	55%	51%
Potassium carbonate	K ₂ CO ₃	-	42%
Magnesium chloride	MgCl ₂ 6 H ₂ O	33%	26%
Lithium chloride	LiCl	12%	10%
Silica gel	SiO ₂	3%	3%

112 **3.3. Sample preparation**

113 Characterization of the sorption isotherm using the gravimetric method requires long-term
114 experiments due to the samples dimensions and water transfer properties of the materials
115 tested. In order to reduce the experiment duration the samples used usually have small
116 dimensions: thin slices [15-17], powders [18-20], crushed or sawn small specimens (up to
117 one centimetre max) [4; 6; 20-22]. One can note that such sample shape and dimensions
118 greatly differ from a concrete Representative Volume Element (RVE). In addition, if the
119 sample preparation has an effect on the experiments (for instance superficial microcracking

120 or carbonation) then this effect may concern a great part of the sample volume because of its
121 thinness.

122 In this study an attempt was made to use massive samples as close as possible to a RVE.
123 Hence “massive” cylindrical specimens with diameter and height equal to 40 mm were used.
124 One could note that this dimension is far from the minimum 100 mm recommended in the
125 European standard EN 123901 [23], nevertheless this value appeared as the best
126 compromise between the duration of the experiments and the representativeness of the
127 samples (the weight of the resulting samples was about 120 grams.)

128 The samples were cored from 11 cm x 22 cm specimens cured under water (with added
129 lime) at 20°C at least one year after casting. All the samples were taken from the same batch
130 (the one used for the characterisation whose results are presented in Tab. 2). No
131 preventative measure was taken to prevent carbonation since it is expected to affect only a
132 small zone at the surface of the samples that is to say a negligible volume when compared to
133 the total volume of the samples.

134 **3.4. Dry and saturated states**

135 The reference dry state is essential for the correct evaluation of the sorption curves. It is
136 generally estimated using oven-drying. This treatment is known to be too aggressive for
137 cement-based materials (microcracking and modification of pore network) and alternate
138 techniques do exist (isothermal drying using hydrophilic compounds, solvent exchange, D- or
139 P-drying...) [24-29]. Yet as far as only desorption is concerned (no preliminary drying and no
140 further resaturation) oven-drying at 105°C was chosen as the reference dry state.

141 The initial saturated state was achieved using the one-year cure under water (with lime to
142 prevent carbonation). No other specific procedure was used (for instance resaturation using
143 vacuum).

144 **3.5. Experimental protocol**

145 The best method for the characterisation of the first desorption isotherm consists in
146 submitting a unique set of initially saturated samples to decreasing RH steps and waiting for
147 equilibrium for each step [5; 7; 20; 30; 31]. This method was inappropriate for this study
148 given that the time needed to reach equilibrium was expected to be too long due to the
149 massive samples used. It was then decided to use different set of samples to be submitted to
150 a unique RH. The number of sample set for each temperature (30°C and 80°C) was equal to
151 the number of salt solutions (10 sets for each temperature including deionised water and
152 silica gel, see Tab. 4). This method allowed the simultaneous determination of each point of
153 the curve and a corresponding estimated reduction of the experiments time by a factor 10. It
154 was however expected to induce some variability since different specimens were to be used.



155 Fig. 3. View of the 40 mm x 40 mm samples and the climatic boxes containing the saturated
156 salt solutions. Note the opening at the top of the containers which allows inserting a probe for
157 verification of both temperature and RH.

158 The 40 mm x 40 mm cylinder samples were weighed in air and under water before the
159 beginning of the experiments and their volume and saturated density were computed
160 (weighing was carried out using a 1 mg accurate device). They were then put in hermetic

161 containers by groups of three above the saturated salt solutions and the containers were
162 kept in two different ovens regulating the temperature to 30°C and 80°C. A view of the
163 40 mm x 40 mm samples and of the hermetic containers is presented in Fig. 3. The
164 containers were opened periodically to measure the mass of the samples. The latter were left
165 as long as possible in the containers in order to get as close as possible to equilibrium.

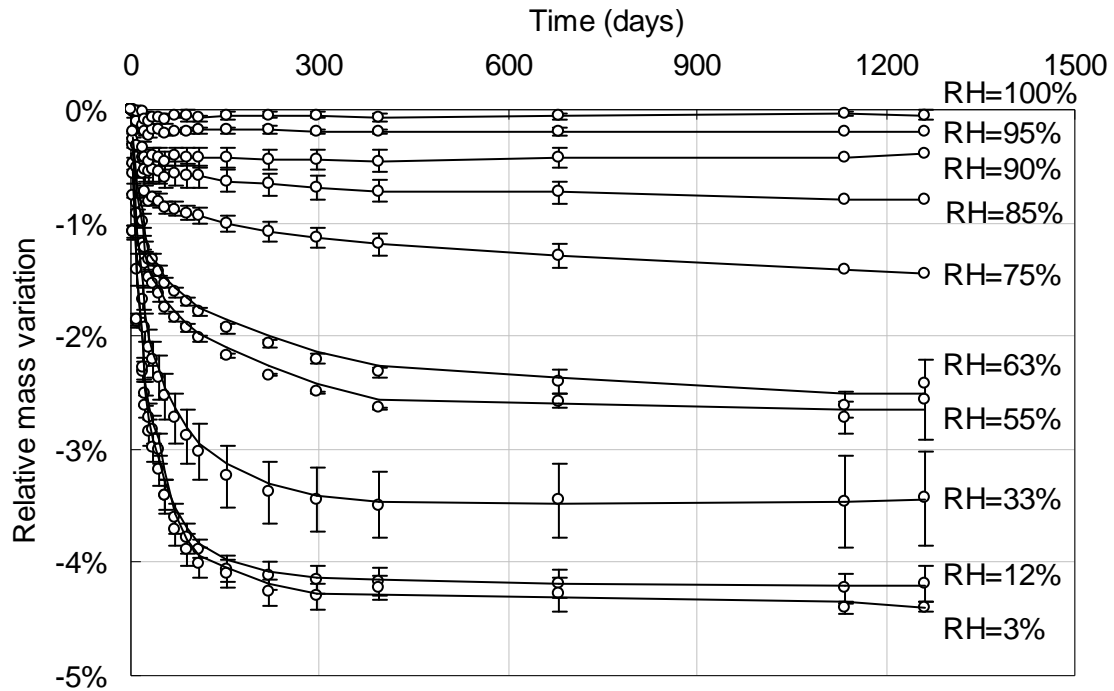
166 **4. Experimental results**

167 **4.1. Mass variation and water transfer properties**

168 On the basis of the periodic mass measurements, the mean relative mass variation ($\Delta m/m$)
169 of the samples for each temperature and RH could be computed following the classical
170 relation:

$$171 \left(\frac{\Delta m}{m} \right)(t) = \frac{m(t) - m_0}{m_0}, \quad (1)$$

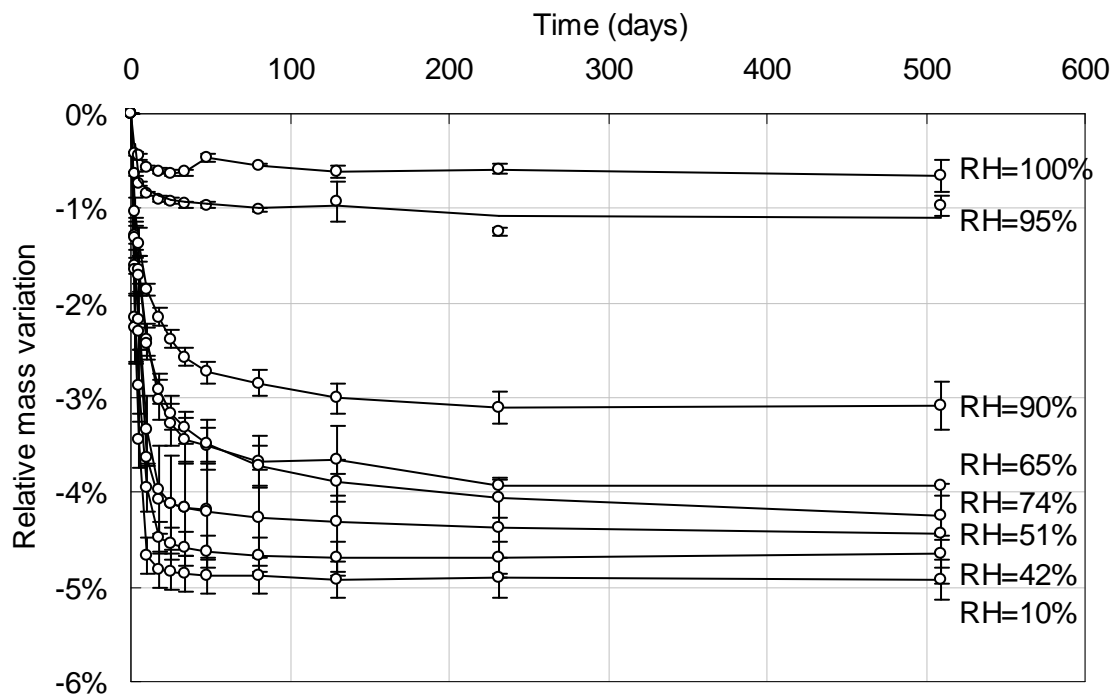
172 where m_0 and $m(t)$ are the initial sample mass (saturated) and the mass for the time t . The
173 results are presented in Fig. 4 and Fig. 5 for 30°C and 80°C respectively.



174

175 Fig. 4. Mass variation of the samples kept at 30°C (each value is the average value obtained

176 using three samples, the error bar stands for the standard deviation).



177

178 Fig. 5. Mass variation of the samples kept at 80°C (each value is the average value obtained

179 using three samples, the error bar stands for the standard deviation).

180 The desorption experiments spanned over 1200 days and 500 days for 30°C and 80°C
 181 respectively. Such experiment durations (qualitatively) appear to be sufficient to reach
 182 equilibrium at 80°C but not at 30°C for which the samples kept between 55% and 85% still
 183 present mass variation after 1200 days. Nevertheless, the amount of water in excess (with
 184 respect to the equilibrium to be reached) is expected to be low and the corresponding error
 185 negligible. One can note that for each temperature the patterns are similar: the mass loss
 186 kinetics is maximal in the early days, it is then continuously reduced as far as the drying
 187 proceeds and the equilibrium is approached. In addition, the lower the RH the higher the
 188 mass loss. The main differences between the results for both temperatures lie in the mass
 189 loss kinetics and in the value reached at equilibrium (the last point will be discussed in the
 190 next chapter).

191 When examining Fig. 4 and Fig. 5 it is obvious that the time needed to reach the equilibrium
 192 at 80°C is much lower than the one needed at 30°C. For instance, the time needed to reach
 193 90% of the mass loss is about one month at 80°C; it is extended to more than one year at
 194 30°C. This point has already been studied by several authors who showed the drying
 195 acceleration and the increase of the water transfer properties with temperature [32-36].

196 **4.2. First desorption isotherms**

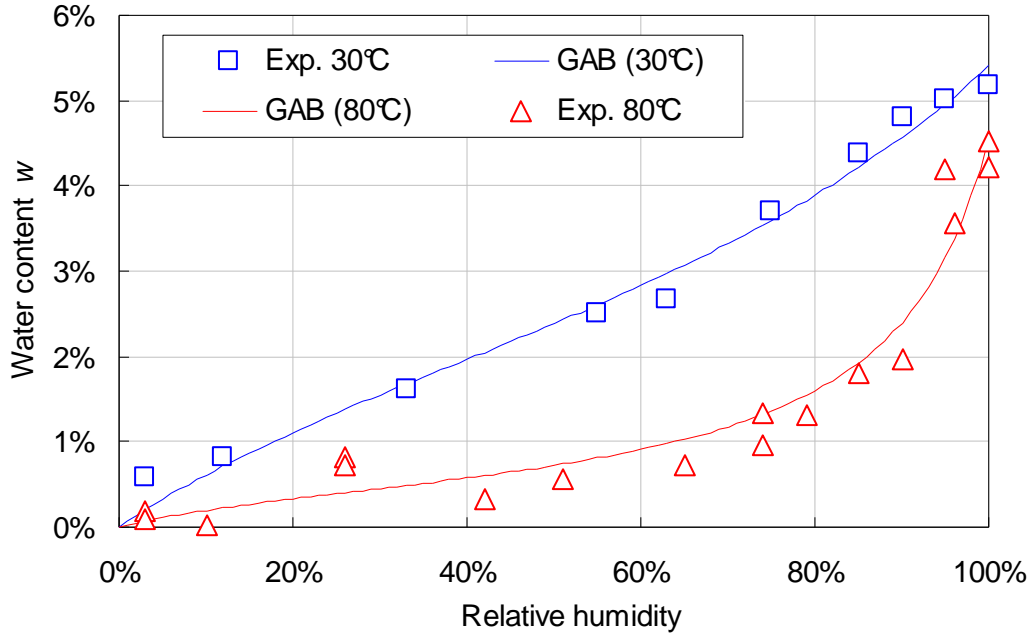
197 In order to determine the first desorption isotherms at 30°C and 80°C, the amount of water
 198 retained according to the RH was expressed using the mass water content w :

$$199 \quad w(T, RH) = \frac{m_w(T, RH)}{m_s}, \quad (2)$$

200 where m_w and m_s are the mass of adsorbed water and the mass of the dry material
 201 respectively. It was computed using the experimental mass variations ($\Delta m/m$):

$$202 \quad w(T, RH) = \frac{d_{sat}}{d_{sat} - \phi} \left[\left(\frac{\Delta m}{m} \right) (T, RH) + \frac{\phi}{d_{sat}} \right], \quad (3)$$

203 where d_{sat} and ϕ are the saturated initial density and the porosity respectively. The results are
 204 presented in Fig. 6, the reference dry state was fixed using oven drying at 105°C; that is to
 205 say the value of the porosity ϕ needed in eq. (3) is equal to 12.3%.



206
 207 Fig. 6. First desorption isotherms at 30°C and 80°C.

208 The symbols stand for the experimental results derived from the experiments whereas the
 209 solid lines stand for a curve-fitting using the GAB model [37-39]. The GAB model is a three-
 210 parameter which is an evolved version of the BET model (with a supplementary parameter
 211 k), it can be written as follows:

$$212 \quad w(h) = \frac{Ckw_m h}{(1 - kh)[1 + (C - 1)kh]}, \quad (4)$$

213 where C , k and w_m are the three parameters of the GAB model and h is the relative humidity.
 214 The GAB model is used here because it is based on physical phenomena (which yield a
 215 correct isotherm shape), it was shown that it can be used almost over the whole RH range
 216 and offers the best fit among various adsorption models [37; 40-43]. Moreover this model is
 217 widely used in various fields and it has already proven its suitability for cementitious
 218 materials [44-46]. The values of the three parameters of the GAB model are reported in Tab.
 219 5.

220 Tab. 5. Data for the fitting of the GAB model at 30°C and 80°C.

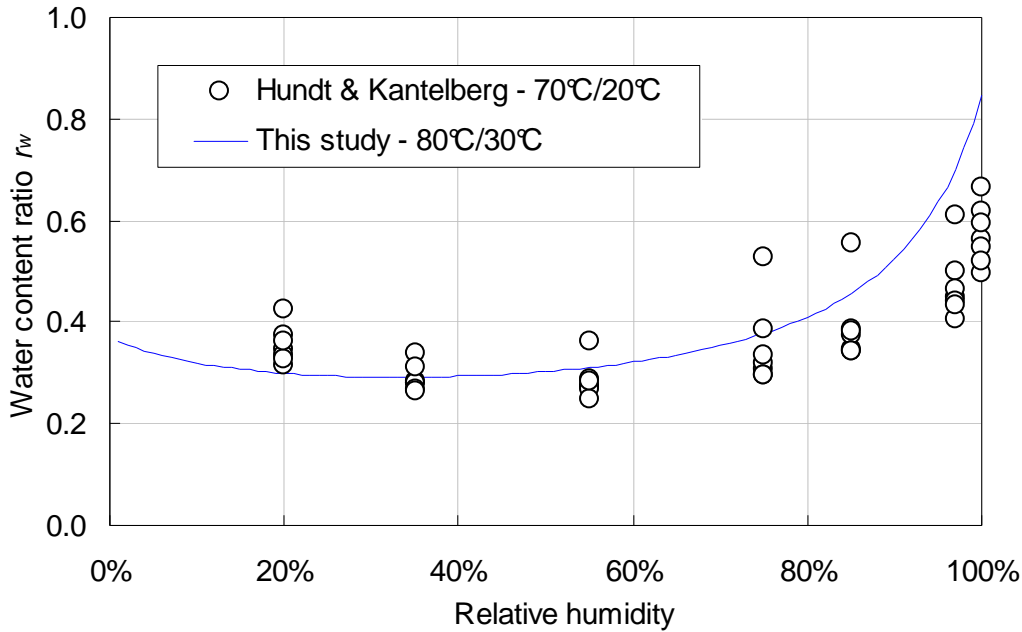
Temperature	C [-]	k [-]	w_m [kg/kg]
30°C	4.690	0.592	2.534%
80°C	6.010	0.897	0.480%

221
 222 Looking at Fig. 6, one can easily notice that temperature has a tremendous impact on the
 223 first desorption isotherm: at 30°C the curve can almost be described by a straight line from
 224 the origin up to the saturation point ($w \approx 5.4\%$) whereas at 80°C high non-linearity appears.
 225 In addition to the alteration of the curve morphology, one can note that for a given RH the
 226 water content at equilibrium is always reduced at 80°C (when compared to the values
 227 obtained at 30°C). This effect even appears for RH= 100%: an initially saturated sample
 228 whose temperature is suddenly increased up to 80°C undergoes a significant mass loss:
 229 from 5.4% to 4.6%. The reduction of the water content at equilibrium is not constant over the
 230 whole RH range; for instance for RH=100% the difference in the water content is about 0.8%
 231 (absolute value) whereas it is about 2.3% for RH=80%. This effect can be, for instance,
 232 quantified using the water content ratio (by mass) r_w :

$$r_w(RH, T) = \frac{w(T, RH)}{w(30^\circ\text{C}, RH)} \quad (5)$$

233
 234 Fig. 7 presents the evolution of the water content (by mass) r_w as a function of RH for the
 235 experiments presented in this study. Data derived from the work of Hundt & Kantelberg [7]
 236 are also presented; in this case the two temperatures were 20°C and 70°C, and different
 237 cementitious materials were used (hardened cement pastes with different W/C, mortar and
 238 concrete with different cures or preconditioning methods). Despite these differences, one can
 239 note that the results obtained in this study are in good agreement with the results of Hundt &
 240 Kantelberg. The water content ratio appears not to be constant over the full RH range: the
 241 general shape of the curve is parabolic and thus presents a minimum value of about 0.3
 242 which is roughly located at RH=35%. The maximal value of the ratio $r_w=0.85$ is reached at
 243 saturation (for RH=100%). This fact is very important, because it means that the saturation
 244 state is not constant versus temperature. It implies that a saturated concrete becomes

245 oversaturated when the temperature increases. As a consequence the concrete is out of
 246 equilibrium and water is released and evacuated into the environment: this phenomenon can
 247 clearly be seen on Fig. 5 on which the mass loss of saturated samples kept at RH=100% and
 248 80°C can be seen whereas saturated samples kept at 30°C and RH=100% do not exhibit
 249 such behaviour (Fig. 4).



250
 251 Fig. 7. Evolution of the water content ratio r_w as a function of RH.

252 4.3. Pore structure investigation

253 In order to quantify the influence of temperature on the first desorption isotherm, the specific
 254 surface area S_{BET} was estimated using the BET model [47]:

$$255 \quad w = \frac{Cw_m h}{(1-h)[1+(C-1)h]}, \quad (6)$$

256 where C and w_m are two positive parameters of the BET model. w_m is the mass of water (for
 257 one gram of dried material) needed to complete a monomolecular adsorbed layer, its value is
 258 used to compute the specific surface area S_{BET} . According to the recommendations of the
 259 IUPAC [48] the BET parameters were not estimated using the experimental data from the full
 260 RH range. However, due to the lack of experimental data in the low RH (typically between
 261 5% and 30%) the fitting interval was extended up to RH=50%. In so doing, it was accepted

262 that this would not yield an accurate value of the specific surface, rather only a rough
 263 estimate. The fitted parameters are reported in Tab. 6.

264 Tab. 6. Data for the fitting of the BET model.

Temperature	30°C	80°C
C [-]	20.8	22.0
w_m [m ³ /kg]	1.16%	0.35%
S_{BET} [m ² /g]	41	13

265 The specific surface area S_{BET} was estimated using [49]:

$$266 \quad S_{BET}(T) = w_m(T) \frac{A_w}{\rho_w V_w}(T) N_A, \quad (7)$$

267 where V_w and N_A are the molar volume of water ($0.1808 \cdot 10^{-4}$ m³/mol and $0.1853 \cdot 10^{-4}$ m³/mol
 268 at 30°C and 80°C respectively) and Avogadro's number ($N_A = 6.02 \cdot 10^{23}$) and A_w is the area
 269 occupied by a single water molecule on the surface of the sample. The latter was estimated
 270 using the equation [50; 51]:

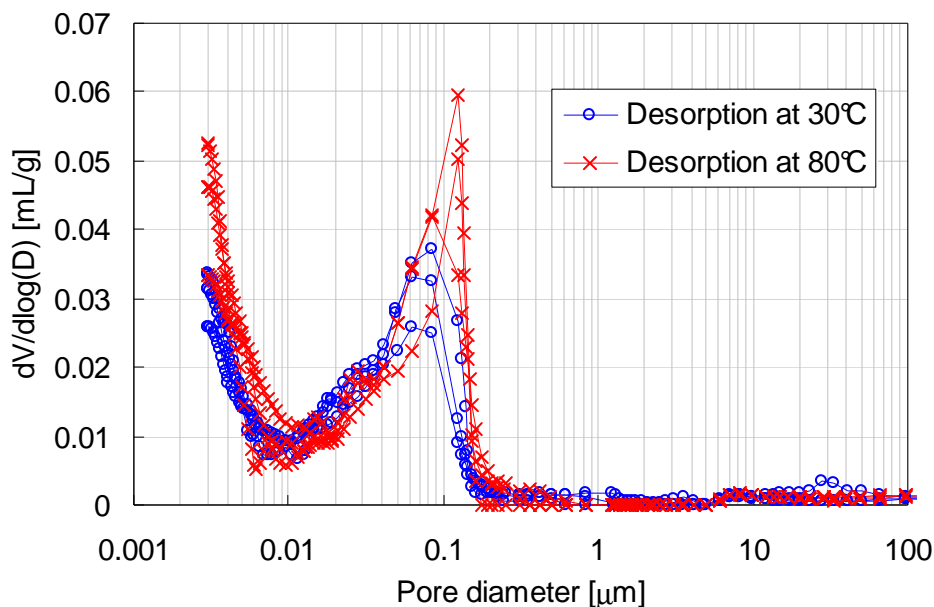
$$271 \quad A_w(T) = 1.091 \left[\frac{M_w}{N_A \rho_w(T)} \right]^{\frac{2}{3}}, \quad (8)$$

272 where M_w is the molar mass of water ($18 \cdot 10^{-3}$ kg/mol). The resulting coverage areas for one
 273 molecule of water A_w are 10.538 \AA^2 and 10.712 \AA^2 at 30°C and 80°C respectively. These
 274 values are very close to 10.508 \AA^2 used by Baroghel-Bouny (for 23°C). Many different values
 275 were used to calculate S_{BET} in the literature (ranging from 10.5 \AA^2 to 12.5 \AA^2) leading to
 276 discrepancies in the specific surface area estimations and major difficulties of comparison
 277 between all the published results [46; 52]. All the data used for the estimation (V_m and A_w in
 278 particular) are however reported here which allows to estimate S_{BET} using different data.

279 The specific surface area obtained at 30°C: the result is $S_{BET}(30^\circ\text{C}) = 41 \text{ m}^2/\text{g}$. This value is
 280 consistent with the data published (using water vapour): roughly ranging from 20 to 200 m²/g
 281 according to the cementitious material tested and the technique used [15; 22; 29; 52-57]. The
 282 value of the specific surface area S_{BET} is divided by 3 when measured at 80°C and falls down
 283 to $S_{BET}(80^\circ\text{C}) = 13 \text{ m}^2/\text{g}$ (Tab. 6). These data are comparable to the results obtained by Bray
 284 & Sellevold [58] and Radjy & Richards [19] who showed that a temperature increase

285 between ambient temperature and 90°C or 100°C resulted in a decrease of the BET
286 monolayer parameter V_m estimated using water desorption experiments (and thus the
287 specific surface area S_{BET}).

288 In the same time, Mercury intrusion porosimetry (MIP) experiments were performed to
289 highlight the influence of the desorption temperature on pore size distribution. The samples
290 used for the desorption experiments at 30°C and 80°C and kept at RH=3% were used. They
291 were crushed into small parts (several millimetres), frozen by immersion into liquid nitrogen,
292 let to dry under vacuum for seven days and then tested at ambient temperature. The results
293 are presented on Fig. 8. One can see that for the two desorption temperatures a bi-modal
294 pore size distribution is obtained corresponding to C-S-H nanoporosity (around 3 nm) and
295 capillary porosity (around 100 nm). For desorption at 30°C, the access diameter for capillary
296 porosity is about 70 nm. Desorption at 80°C appears to slightly shift it towards larger
297 diameters (110 nm) as it was already shown [25; 59]. The variability observed in the intruded
298 volume was not thought to be significant and assumed to be related to the presence of sand
299 and aggregates in the samples together with hardened cement paste.



300

301 Fig. 8. Pore size distributions obtained by MIP after desorption at 30°C and 80°C.

302 The specific surface areas estimated using MIP were quite different from the ones derived
303 from desorption. A value of about 10 m²/g after desorption at 30°C was obtained; the same
304 value (12 m²/g) was obtained for desorption at 80°C in contradiction with desorption results.

305 **5. Discussion**

306 The (slight) increase of the capillary porosity average access diameter between 30°C and
307 80°C observed using MIP as well as the decrease of the specific surface area are consistent
308 with the desorption isotherm modification: the coarser the pore size, the greater the upward
309 deviation (see for instance [22] for compacted cement pastes; [56; 60] for hardened cement
310 pastes with variable water-to-cement ratio and [61-65] for compacted powders.) Yet one
311 must note that the porosity increase (between 30°C and 80°C, Tab. 3) is not compatible with
312 the fall of the water content at saturation (it is expected to induce a water uptake at saturation
313 leading to mass gain.) The latter may be explained by the decrease of water density when
314 temperature is increased.

315 However these two phenomena are believed by the author to have a small impact on the
316 isotherms: the decrease of water density (at least between 20°C and 80°C) as well as the
317 coarsening of the pore structure as observed using MIP remain very limited. In the author's
318 mind, these two phenomena cannot explain the important modifications of the desorption
319 isotherm observed between 30°C and 80°C. Moreover the difference of specific surface
320 areas obtained using the 80°C isotherm and MIP led the author think that another
321 phenomenon directly linked to temperature might be at work.

322 Such a phenomenon can be described as follows: adsorption is an exothermic process [66;
323 67] and according to the principle of Le Chatelier and the rule of Van't Hoff: the effect of a
324 change in temperature on a system at equilibrium is to shift the equilibrium in the direction
325 that acts to counteract and nullify the temperature change. This means increasing
326 temperature hinders adsorption and promotes desorption; as a consequence a lesser
327 number of molecules can be adsorbed. This phenomenon is very well-known in adsorption
328 science. Many studies can be found in the literature which show the impact of temperature

329 on sorption isotherms for different adsorbents and adsorbates [50; 68-73], the results always
 330 show the same modifications of the sorption isotherms as described in this paper.
 331 Furthermore in adsorption technology, the temperature increase and the heat transfers
 332 induced by the heat of adsorption are accounted for the design of the adsorbent beds (to
 333 avoid the performance reduction due to temperature increase) and thermal treatments at
 334 elevated temperature are usually used as a method to regenerate adsorbents (this method is
 335 also know as “temperature swing adsorption”) [73; 74].

336 This effect can be described using the Clausius-Clapeyron equation which permits the
 337 evaluation of the heat involved in a change of phase for a system in equilibrium, in the case
 338 of adsorption it can written under the form [66]:

$$339 \quad Q_{st}(w) = -R \left[\frac{\partial \ln(p_v)}{\partial \left(\frac{1}{T} \right)} \right]_w, \quad (9)$$

340 where Q_{st} is the isosteric heat of adsorption [J/mol], T and R are the absolute temperature [K]
 341 and the universal gas constant ($R = 8.3145$ J/mol/K) and p_v is the water vapour pressure [Pa]
 342 at equilibrium with the adsorbed quantity w respectively. In our case the heat of adsorption
 343 could be estimated using the two isotherms obtained at 30°C and 80°C using the integrated
 344 form of eq. (9):

$$345 \quad Q_{st}(w) = -R \frac{T_1 T_2}{T_1 - T_2} \ln \left[\frac{p_v(T_1, w)}{p_v(T_2, w)} \right], \quad (10)$$

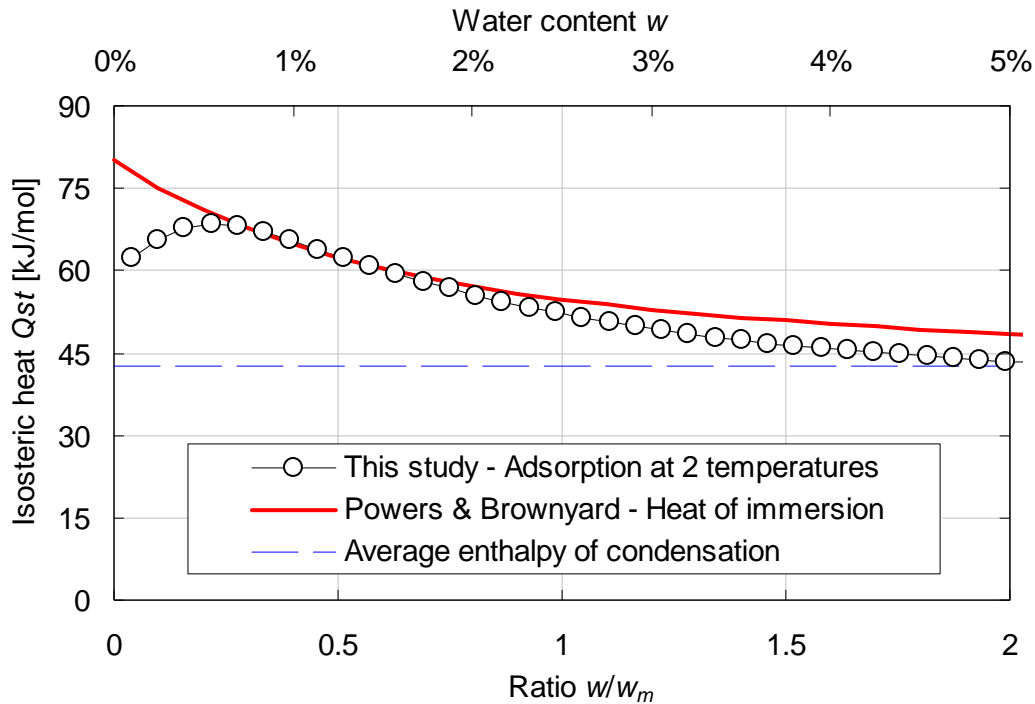
346 where $p_{v1}(w)$ and $p_{v2}(w)$ are the vapour pressures at equilibrium with the water content w for
 347 the temperatures T_1 and T_2 respectively. In so doing, it was implicitly assumed that the pore
 348 size distribution and the water properties remain constant over the whole temperature range.
 349 Fig. 9 presents the resulting evolution of the isosteric heat of desorption as a function of
 350 water content. One can see that the isosteric heat of desorption is a decreasing function of
 351 water content: the high value observed for low water contents is representative of strong
 352 bonding between the adsorbed water molecules and the cementitious substrate whereas the
 353 decrease can be related to the drop of the influence of the substrate with the increase of the
 354 distance between adsorbed water molecules and substrate. The value reached at high water

355 contents is equal to the average enthalpy of condensation (42.7 kJ/mol between 30 and
356 80°C): it can be considered that there is no more influence of the substrate and water
357 molecules are bound the ones to the others (condensation).

358 For verification purpose, the isosteric heat of desorption obtained in this study was compared
359 to the one proposed by Powers & Brownyard [60]. They used the heat-of-solution method on
360 two hardened cement pastes. The method consists in dissolving paste samples in a
361 calorimeter and measuring the heat evolved. Repeated measurements on samples
362 contained different amounts of adsorbed water allowed them to evaluate the isosteric heat of
363 adsorption which can be written under the following form (in kJ/mol):

$$364 \quad Q_{st}(w) = L + \frac{64.6}{(1.31 + w/w_m)^2}, \quad (11)$$

365 where $L = 42.7$ kJ/mol is the average condensation enthalpy of water within the range 30-
366 80°C. The comparison is presented on Fig. 9. One can see that except for low values of
367 w/w_m (below 0.2), there is a good agreement between the two curves. This fact is important
368 since Powers & Brownyard performed their experiments at constant (ambient) temperature.
369 This seems to indicate that the two phenomena initially identified to explain the influence of
370 temperature (coarsening of the pore structure and water properties evolution) might be
371 negligible in front of the desorption induced by temperature.

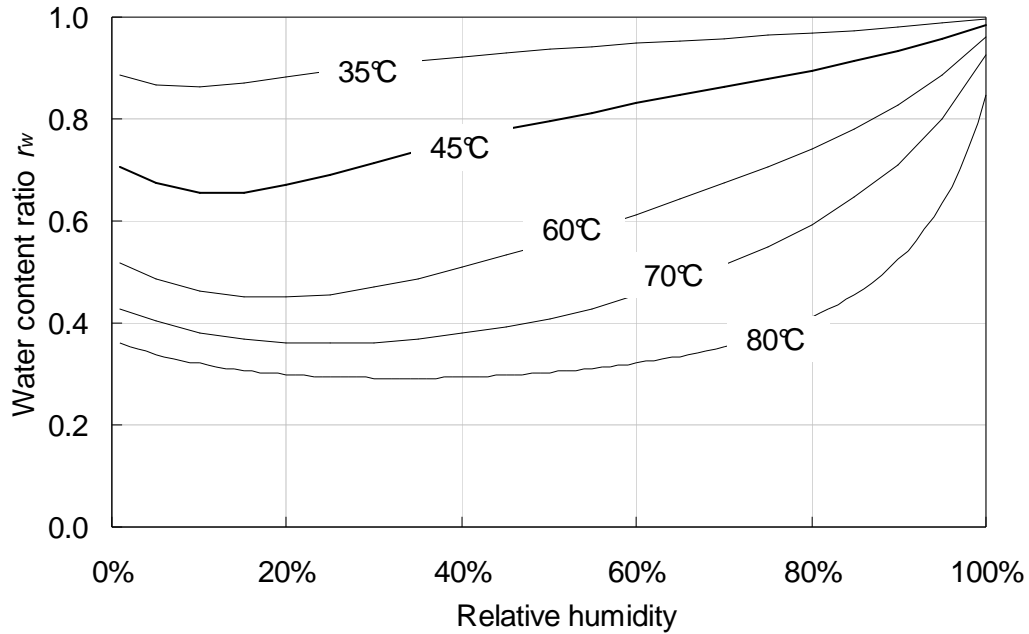


372

373 Fig. 9. Comparison between the isosteric heat of desorption obtained in this study (two
 374 isotherms at two different temperatures and Clausius-Clapeyron) and the one proposed by
 375 Powers & Brownyard using heat-of-solution tests (at ambient temperature).

376 Using Clausius-Clapeyron and the corresponding isosteric heat of desorption, it is possible to
 377 estimate the water content ratio $r_w(RH, T)$ (as defined in eq. (5)) for any arbitrary temperature.

378 Fig. 10 presents the results obtained for temperatures ranging from 35°C to 80°C. One can
 379 see that the fall of water content increases with temperature and whatever the temperature,
 380 the first desorption isotherm is expected to be modified: there is no threshold temperature.
 381 Moreover, the change depends on the temperature level: for a small temperature increase
 382 only the low-RH part of the isotherm is expected to be influenced whereas the isotherm is
 383 expected to be modified over the whole RH range for higher temperatures.



384

385 Fig. 10. Evolution of the ratio $r_w(RH, T)$ as a function of temperature and relative humidity.

386 6. Conclusion

387 In the framework of radioactive waste management and especially in the case of interim
 388 storage, concrete structures should be submitted to temperature up to 80°C and subsequent
 389 drying. The durability assessment of such structures in such unusual conditions thus requires
 390 the knowledge of the first desorption isotherm at 80°C. An experimental campaign was thus
 391 undertaken to characterize the first desorption isotherms (at 30°C and 80°C) of a French
 392 reference concrete for radioactive waste management. This was done using the desiccator
 393 method with massive samples. The results showed an important impact of temperature on
 394 the first desorption isotherm:

- 395 1. the general shape of the isotherm is modified and leads to more pronounced
 396 non-linearities;
- 397 2. the water content at equilibrium is drastically reduced at 80°C over the whole RH
 398 range;
- 399 3. the water content at saturation at 80°C is significantly lower than at 30°C.

400 The examination of the results led the author to think that the coarsening of the pore
401 structure and the evolution of water properties could not explain these important
402 modifications and that another phenomenon was at work. The latter consists in desorption
403 induced by temperature and can be described using Clausius-Clapeyron formula. Using the
404 two isotherms acquired, it was possible to evaluate the isosteric heat of desorption and to
405 compare it to the data obtained by Powers & Brownyard using a different method at constant
406 temperature. The two of them are in good agreement. This seems to indicate that the
407 temperature induced desorption is the predominant phenomenon in our experiments (for
408 temperatures less than 80°C.)

409 **7. Acknowledgements**

410 This work was part of a project funded by Electricité de France (EdF) and the French agency
411 for radioactive waste management (Andra). The author would like to thank Xavier Bourbon
412 (Andra/DS) and Yann Le-Pape (EdF/DER) for their scientific support and also Guillaume
413 Ranc who has initiated this study, Philippe Pétrini for his help in preparing and performing the
414 experiments. Profitable discussions with Sébastien Charles and Christophe Gallé are
415 gratefully acknowledged.

416 **8. References**

- 417 [1] H. Lagrave, Dossier de définition pour l'entreposage de longue durée des déchets
418 HAVL et des combustibles usés (in french), CEA Internal Report DTEC/2005/10
419 (2005) 55p.
- 420 [2] H. Lagrave, Dossier de définition de l'entreposage de longue durée des déchets
421 MAVL ou de catégorie B (in french), CEA Internal Report DTEC/2005/11 (2005) 63p.
- 422 [3] J.-F. Daïan, Processus de condensation et de transfert d'eau dans un matériau méso
423 et macroporeux - Etude expérimentale du mortier de ciment (in french), Ph-D Thesis,
424 Institut National Polytechnique de Grenoble (INPG), 1986, 319p.p.
- 425 [4] J.-F. Daïan, Condensation and isothermal water transfer in cement mortar, part I -
426 pore size distribution, equilibrium, water condensation and imbibition, *Transport in*
427 *Porous Media* 3(6) (1988) 563-589.
- 428 [5] F. Radjy, E.J. Sellevold, K.K. Hansen, Isosteric vapor pressure-temperature data for
429 water sorption in hardened cement paste: enthalpy, entropy and sorption isotherms at
430 different temperatures, Report BYG-DTU R057, Technical University of Denmark
431 (DTU), Lyngby, Denmark, 2003, 58p.

- 432 [6] T. Ishida, K. Maekawa, T. Kishi, Enhanced modeling of moisture equilibrium and
433 transport in cementitious materials under arbitrary temperature and relative humidity
434 history, *Cement and Concrete Research* 37(4) (2007) 565-578.
- 435 [7] J. Hundt, H. Kantelberg, Sorptionsuntersuchungen an zementstein, zementmörtel und
436 beton (in german), *Deutscher Ausschuss für Stahlbeton Heft 297* (1978) 25-39.
- 437 [8] Z.P. Bažant, W. Thonguthai, Pore pressure and drying of concrete at high
438 temperature, *Journal of the Engineering Mechanics Division (ASCE)* 104(5) (1978)
439 1059-1079.
- 440 [9] Z.P. Bažant, J.C. Chern, W. Thonguthai, Finite element program for moisture and
441 heat transfer in heated concrete, *Nuclear Engineering & Design* 68(1) (1980) 61-70.
- 442 [10] Z.P. Bažant, W. Thonguthai, Pore pressure in heated concrete walls - theoretical
443 prediction, *Magazine of Concrete Research* 31(107) (1979) 67-76.
- 444 [11] B. Bary, A polydispersed particle system representation of the porosity for non-
445 saturated cementitious materials, *Cement and Concrete Research* 36(11) (2006)
446 2061.
- 447 [12] L.J. Klinkenberg, The permeability of porous media to liquid and gases, *American
448 Petroleum Institute, Drilling and Production Practice* (1941) 200-214.
- 449 [13] CEN, Hygrothermal performance of building materials and products - Determination
450 of hygroscopic sorption properties, *European Committee for Standardization (CEN),
451 European Standard EN ISO 12571* (2000) 17p.
- 452 [14] OIML, The scale of relative humidity of air certified against saturated salt solutions,
453 *International Organization of Legal Metrology (OIML), Recommendation R 121* (1996)
454 12p.
- 455 [15] V. Baroghel-Bouny, Water vapour sorption experiments on hardened cementitious
456 materials: Part I. Essential tool for analysis of hygral behaviour and its relation to pore
457 structure, *Cement and Concrete Research* 37(3) (2007) 414-437.
- 458 [16] Xu Aimin, Water desorption isotherms of cement mortar with fly ash, *Nordic Concrete
459 Research* 8 (1989) 9-23.
- 460 [17] R.M. Espinosa, L. Franke, Influence of the age and drying process on pore structure
461 and sorption isotherms of hardened cement paste, *Cement and Concrete Research*
462 36(10) (2006) 1969-1984.
- 463 [18] V. Baroghel-Bouny, B. Perrin, L. Chemloul, Détermination expérimentale des
464 propriétés hydriques des pâtes de ciment durcies - Mise en évidence des
465 phénomènes d'hystérésis (in french), *Materials and Structures* 30(6) (1997) 304-348.
- 466 [19] F. Radjy, C.W. Richards, Effect of curing and heat treatment history on the dynamic
467 mechanical response and the pore structure of hardened cement paste, *Cement and
468 Concrete Research* 3(1) (1973) 7-21.
- 469 [20] V. Baroghel-Bouny, M. Mainguy, T. Lassabatere, O. Coussy, Characterization and
470 identification of equilibrium and transfer moisture properties for ordinary and high-
471 performance cementitious materials, *Cement and Concrete Research* 29(8) (1999)
472 1225-1238.
- 473 [21] S. Tada, K. Watanabe, Dynamic determination of sorption isotherm of cement based
474 materials, *Cement and Concrete Research* 35(12) (2005) 2271-2277.
- 475 [22] R.S. Mikhail, G.A. Oweimreen, Surface area and pore structure of compressed low-
476 porosity cement pastes, *Cement and Concrete Research* 3(5) (1973) 561-573.
- 477 [23] CEN, Testing hardened concrete, part I: shape, dimensions and other requirements
478 for test specimens and moulds, *European Committee for Standardization, European
479 Standard EN 12390-1* (2001) 10p.
- 480 [24] J.J. Beaudouin, B.T. Tamtsia, Effect of drying methods on microstructural changes in
481 hardened cement paste: an A.C. impedance spectroscopy evaluation, *Journal of
482 Advanced Concrete Technology* 2(1) (2004) 113-120.
- 483 [25] C. Gallé, Effect of drying on cement-based materials pore structure as identified by
484 mercury intrusion porosimetry. A comparative study between oven-, vacuum-, and
485 freeze-drying, *Cement and Concrete Research* 31(10) (2001) 1467-1477.

- 486 [26] G.G. Litvan, Variability of the nitrogen surface area of hydrated cement paste,
487 Cement and Concrete Research 6(1) (1976) 139-144.
- 488 [27] J.J. Beaudouin, J. Marchand, Pore structure, in: V.S. Ramachandran and J.J.
489 Beaudouin (Eds), Handbook of analytic techniques in concrete science and
490 technology, Noyes Publications, Park Ridge, USA, 2001, 528-628.
- 491 [28] M.C. Garci Juenger, H.M. Jennings, The use of nitrogen adsorption to assess the
492 microstructure of cement paste, Cement and Concrete Research 31(6) (2001) 883-
493 892.
- 494 [29] A. Korpa, R. Trettin, The influence of different drying methods on cement paste
495 microstructures as reflected by gas adsorption: comparison between freeze-drying,
496 D-drying, P-drying and oven-drying, Cement and Concrete Research 36(4) (2006)
497 634-649.
- 498 [30] J. Adolphs, A. Schreiber, Microstructural characterization of Ultra-High Performance
499 Concrete, in: M. Schmidt, E. Fehling and C. Geisenhanslüke (Eds), Proceedings of
500 the International Symposium on Ultra-High Performance Concrete, Kassel
501 (Germany), Kassel University, 2004, 265-271.
- 502 [31] I. Pane, W. Hansen, Surface characteriation of blended cements by H₂O and N₂
503 sorption isotherms, in: J. Weiss, K. Kovler, J. Marchand and S. Mindess (Eds),
504 Proceedings of the the 1st International Symposium on Advances in Concrete through
505 Science and Engineering, Chicago, USA, RILEM PRO048, 2004.
- 506 [32] B.P. Hughes, I.R.G. Lowe, J. Walker, The diffusion of water in concrete at
507 temperatures between 50 and 95°C, British Journal of Applied Physics 17(12) (1966)
508 1545-1452.
- 509 [33] N.L. Hancox, The role of moisture diffusion in the drying of cement paste under the
510 influence of temperature gradients, Journal of Physics D: Applied Physics 1(12)
511 (1968) 1769-1777.
- 512 [34] R. Černý, J. Drchalová, P. Rovnaníková, The effects of thermal load and frost cycles
513 on the water transport in two high-performance concretes, Cement and Concrete
514 Research 31(8) (2001) 1129-1140.
- 515 [35] S.F. Wong, T.H. Wee, S. Swaddiwudhipong, S.L. Lee, Study of water movement in
516 concrete, Magazine of Concrete Research 53(3) (2001) 205-220.
- 517 [36] T.C. Powers, H.M. Mann, L.E. Copeland, The flow of water in hardened Portland
518 cement paste, Portland Cement Association Bulletin 106 (1959) 18p.
- 519 [37] R.B. Anderson, Modifications of the Brunauer, Emmett and Teller equation, Journal of
520 the American Chemical Society 68(4) (1946) 686-691.
- 521 [38] C. van der Berg, Vapour sorption equilibria and other water-starch interactions: a
522 physico-chemical approach, Ph-D thesis, Agricultural University of Wageningen, The
523 Netherlands, 1981, 186p.
- 524 [39] S. Brunauer, J. Skalny, E.E. Bodor, Adsorption on non porous solids, Journal of
525 Colloid and Interface Science 30(4) (1969) 546-552.
- 526 [40] P.-N.T. Johnson, J.G. Brennan, Moisture sorption isotherm characteristics of plantain
527 (*Musa*, AAB), Journal of Food Engineering 44(2) (2000) 79-84.
- 528 [41] C.P. McLaughlin, T.R.A. Magee, The determination of sorption isotherm and the
529 isosteric heats of sorption for potatoes, Journal of Food Engineering 35(3) (1998)
530 267-280.
- 531 [42] A. Jonquière, A. Fane, Modified BET models for modeling water vapor sorption in
532 hydrophilic glassy polymers and systems deviating strongly from ideality, Journal of
533 Applied Polymer Science 67(8) (1998) 1415-1430.
- 534 [43] L.-T. Lim, I.J. Britt, M.A. Tung, Sorption and transport properties of water in Nylon 6,6
535 Film, Journal of Applied Polymer Science 71(2) (1999) 197-206.
- 536 [44] Y. Xi, Z.P. Bažant, H.M. Jennings, Moisture diffusion in cementitious materials -
537 Adsorption isotherms, Advanced Cement Based Materials 1(6) (1994) 248-257.
- 538 [45] S. Bonnet, B. Perrin, Influence de la présence des ions chlorures sur les propriétés à
539 l'équilibre de différents mortiers (chloride influence on equilibrium properties of
540 mortars), Materials and Structures 32(7) (1999) 492-499.

- 541 [46] A. Xu, Water desorption isotherms of cement mortar with fly ash, *Nordic Concrete*
542 *Research* 8 (1989) 9-23.
- 543 [47] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers,
544 *Journal of the American Chemical Society* 60(2) (1938) 309-319.
- 545 [48] IUPAC, Commission on Colloid and Surface Chemistry: Reporting physisorption data
546 for gas/solid systems with special reference to the determination of surface area and
547 porosity (Recommendations 1984), *Pure and Applied Chemistry* 57(4) (1985) 603-
548 619.
- 549 [49] J.B. Condon, Surface area and porosity determinations by physisorption -
550 Measurements & theory, Elsevier, 2006, 274p.
- 551 [50] S.J. Gregg, K.S.W. Sing, Adsorption, surface area and porosity, Academic Press,
552 London, United Kingdom, 1982, 303p.
- 553 [51] V. Baroghel-Bouny, Caractérisation des pâtes de ciment et des bétons: Méthodes,
554 analyse, interprétations (in french), Presses du Laboratoire Central des Ponts et
555 Chaussées, Paris, France, 1994, 468p.
- 556 [52] I. Odler, The BET-specific surface area of hydrated Portland cement and related
557 materials, *Cement and Concrete Research* 33(12) (2003) 2049-2056.
- 558 [53] J.J. Thomas, H.M. Jennings, A.J. Allen, The surface area of hardened cement paste
559 as measured by various techniques, *Concrete Science and Engineering* 1(1) (1999)
560 45-64.
- 561 [54] I. Odler, J. Hagymassy, M. Yudenfreund, K.M. Hanna, S. Brunauer, Pore structure
562 analysis by water vapor adsorption. IV. Analysis of hydrated portland cement pastes
563 of low porosity, *Journal of Colloid and Interface Science* 38(1) (1972) 265-276.
- 564 [55] J. Skalny, I. Odler, Pore structure of calcium silicate hydrates, *Cement and Concrete*
565 *Research* 2(4) (1972) 387-400.
- 566 [56] J. Hagymassy, I. Odler, M. Yudenfreund, J. Skalny, S. Brunauer, Pore structure
567 analysis by water vapor adsorption. III. Analysis of hydrated calcium silicates and
568 portland cements, *Journal of Colloid and Interface Science* 38(1) (1972) 20-34.
- 569 [57] R.S. Mikhail, S.A. Abo-El-Enein, Studies on water and nitrogen adsorption on
570 hardened cement pastes I - Development of surface in low porosity pastes, *Cement*
571 *and Concrete Research* 2(4) (1972) 401-414.
- 572 [58] W.H. Bray, E.J. Sellevold, Water sorption properties of hardened cement paste cured
573 or stored at elevated temperatures, *Cement and Concrete Research* 3(6) (1973) 723-
574 728.
- 575 [59] E.J. Sellevold, Mercury porosimetry of hardened cement paste cured or stored at
576 97°C, *Cement and Concrete Research* 4(3) (1974) 399-404.
- 577 [60] T.C. Powers, T.L. Brownyard, Studies of the physical properties of the hardened
578 cement paste, *Portland Cement Association Bulletin* 22 (1948) 356p.
- 579 [61] P.C. Carman, F.A. Raal, Role of capillary condensation in physical adsorption, *Nature*
580 167 (1951) 112-113.
- 581 [62] P.C. Carman, F.A. Raal, Physical adsorption of gases on porous solids I -
582 Comparison between loose powders and porous plugs, *Proceedings of the Royal*
583 *Society of London - Series A, Mathematical and Physical Sciences* 209(1096) (1951)
584 59-69.
- 585 [63] P.C. Carman, Physical adsorption of gases on porous solids II - Calculation of pore-
586 size distribution, *Proceedings of the Royal Society of London - Series A,*
587 *Mathematical and Physical Sciences* 209(1096) (1951) 69-81.
- 588 [64] R.G. Avery, J.D.F. Ramsay, The sorption of nitrogen in porous compacts of silica and
589 zirconia powders, *Journal of Colloids and Interface Science* 42(3) (1973) 597-606.
- 590 [65] S.J. Gregg, J.F. Langford, Study of the effect of compaction on the surface area and
591 porosity of six powders by measurements of nitrogen sorption isotherms, *Journal of*
592 *the Chemical Society - Faraday Transactions I* 73 (1977) 747-759.
- 593 [66] S. Brunauer, The adsorption of gases and vapors - Volume I - Physical adsorption,
594 Princeton University Press, 1945, 511p.

- 595 [67] D. Myers, Surfaces, interfaces and colloids - Principles and applications, John Wiley,
596 New York, USA, 1999, 519p.
- 597 [68] J. Keller, R. Staudt, Gas adsorption equilibria - Experimental methods and adsorption
598 isotherms, Springer Science, Boston, Massachusetts, USA, 2005, 422p.
- 599 [69] A.A. Fomkin, Adsorption of gases, vapors and liquids by microporous adsorbents,
600 Adsorption 11(3) (2005) 425-436.
- 601 [70] I.I. Salame, T.J. Bandosz, Experimental study of water adsorption on activated
602 carbons, Langmuir 15(2) (1999) 587-593.
- 603 [71] I.I. Salame, T.J. Bandosz, Adsorption of water and methanol on micro- and
604 mesoporous wood-based activated carbons, Langmuir 16(12) (2000) 5435-5440.
- 605 [72] D.D. Do, Adsorption analysis: equilibria and kinetics, Series on Chemical Engineering
606 Vol. 2, Imperial College Press, London, United Kingdom, 1998, 913p.
- 607 [73] R.T. Yang, Adsorbents: fundamentals and applications, John Wiley and Sons,
608 Hoboken, New Jersey, USA, 2003, 425p.
- 609 [74] M. Suzuki, Adsorption engineering, Elsevier Science, Amsterdam, The Netherlands,
610 1990, 270p.
- 611
- 612