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# 1 Experimental investigation of the effect of temperature

2 on the first desorption isotherm of concrete

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### 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 principal mechanism rather than microstructure alteration and water properties evolution. 14

# 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 Daïan has 27 experimentally determined the adsorption isotherms of a water-cured mortar at four different temperatures: 20, 35, 45 and 55°C [3; 4]. The samples have been initially dried at 80°C and 28 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.





Fig. 1. Adsorption curves for a mortar between 20℃ and 55℃ after Daïan [4].

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

These facts have already been pointed at by Hundt & Kantelberg [7] who characterised the 55 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.





Fig. 2. First desorption isotherms for a mature mortar for four temperatures ranging from
20℃ to 70℃ 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 highperformance concrete was characterised at 30°C and 80°C. The temperature dependence of 75 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 properties evolution may have negligible effects. 80

### 81 3. Experimental programme

#### 82 **3.1.** *Material tested*

The material used for the experiments was a modern high-performance concrete, the formulation is reported on Tab. 1. It is based on CEM I cement. The water-to-cement ratio (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 <sup>3</sup>
Sand	Calcareous [0-5]	Boulonnais quarry, France	858	kg/m <sup>3</sup>
Gravel	Calcareous [5-12.5]	Boulonnais quarry, France	945	kg/m <sup>3</sup>
Water	-	-	172	L/m <sup>3</sup>
Superplasticizer	Glenium 27	BASF	10	kg/m <sup>3</sup>

The main properties of the concrete have been determined experimentally on samples taken out of the same batch and cured more than one year under water at 20°C. The values obtained are reported on Tab. 2. All the characterization tests were performed on saturated samples at 20°C (except for the gas permeability me asurements and water porosity which implied complete drying at 60°C) and after thermal treatment at 80°C (until constant mass was achieved, residual properties after cooling). The intrinsic permeability to gas (nitrogen) 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℃	30C	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)	2.0·10 <sup>-17</sup>	4.2·10 <sup>-17</sup>	m²
Klinkenberg coefficient	0.13	0.06	MPa
Heat conductivity	2.49	2.09	W/mK

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

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

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

#### 103 **3.2. Technique used**

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

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

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

#### 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 or carbonation) then this effect may concern a great part of the sample volume because of itsthinness.

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.)

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

#### 134 **3.4.** Dry and saturated states

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

The initial saturated state was achieved using the one-year cure under water (with lime to
prevent carbonation). No other specific procedure was used (for instance resaturation using
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 silica gel, see Tab. 4). This method allowed the simultaneous determination of each point of 152 153 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.



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

The 40 mm x 40 mm cylinder samples were weighed in air and under water before the beginning of the experiments and their volume and saturated density were computed (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  $30^{\circ}$ C and  $80^{\circ}$ 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 
$$\left(\frac{\Delta m}{m}\right)(t) = \frac{m(t) - m_0}{m_0},$$
 (1)

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





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).





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 s amples 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 proceeds and the equilibrium is approached. In addition, the lower the RH the higher the 187 188 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  $80^{\circ}$  is much lower than the one needed at  $30^{\circ}$ . For instance, the time needed to reach 193 90% of the mass loss is about one month at  $80^{\circ}$ ; it is extended to more than one year at 194  $30^{\circ}$ . 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].

#### 1964.2.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 
$$w(T, RH) = \frac{m_w(T, RH)}{m_s},$$
 (2)

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

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

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



206

Fig. 6. First desorption isotherms at  $30^{\circ}$  and  $80^{\circ}$ .

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

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

where *C*, *k* and  $w_m$  are the three parameters of the GAB model and *h* is the relative humidity. The GAB model is used here because it is based on physical phenomena (which yield a correct isotherm shape), it was shown that it can be used almost over the whole RH range and offers the best fit among various adsorption models [37; 40-43]. Moreover this model is widely used in various fields and it has already proven its suitability for cementitious materials [44-46]. The values of the three parameters of the GAB model are reported in Tab. 5. Tab. 5. Data for the fitting of the GAB model at  $30^{\circ}$  and  $80^{\circ}$ .

221

Temperature	C [-]	k[-]	w <sub>m</sub> [kg/kg]
30°C	4.690	0.592	2.534%
<b>3</b> 08	6.010	0.897	0.480%

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 al most 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)  $r_w$ :

233 
$$r_w(RH,T) = \frac{w(T,RH)}{w(30^\circ C,RH)}.$$
 (5)

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

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



250



#### 252 **4.3.** Pore structure investigation

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

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

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

- 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.

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

Temperature	30°C	<b>30C</b>
C[-]	20.8	22.0
<i>w<sub>m</sub></i> [m <sup>3</sup> /kg]	1.16%	0.35%
S <sub>BET</sub> [m²/g]	41	13

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

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

where  $V_w$  and  $N_A$  are the molar volume of water (0.1808·10<sup>-4</sup> m<sup>3</sup>/mol and 0.1853·10<sup>-4</sup> m<sup>3</sup>/mol at 30°C and 80°C respectively) and Avogadro's number ( $N_A = 6.02 \cdot 10^{23}$ ) and  $A_w$  is the area occupied by a single water molecule on the surface of the sample. The latter was estimated using the equation [50; 51]:

271 
$$A_{w}(T) = 1.091 \left[ \frac{M_{w}}{N_{A}\rho_{w}(T)} \right]^{\frac{2}{3}},$$
 (8)

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

The specific surface area obtained at 30°C: the result is  $S_{BET}(30^{\circ}C) = 41 \text{ m}^2/\text{g}$ . This value is consistent with the data published (using water vapour): roughly ranging from 20 to 200 m²/g according to the cementitious material tested and the technique used [15; 22; 29; 52-57]. The value of the specific surface area  $S_{BET}$  is divided by 3 when measured at 80°C and falls do wn to  $S_{BET}(80^{\circ}C) = 13 \text{ m}^2/\text{g}$  (Tab. 6). These data are comparable to the results obtained by Bray & Sellevold [58] and Radjy & Richards [19] who showed that a temperature increase between ambient temperature and 90°C or 100°C resulted in a decrease of the BET monolayer parameter  $V_m$  estimated using water desorption experiments (and thus the 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.



301 Fig. 8. Pore size distributions obtained by MIP after desorption at  $30^{\circ}$  and  $80^{\circ}$ .

The specific surface areas estimated using MIP were quite different from the ones derived from desorption. A value of about 10 m<sup>2</sup>/g after desorption at 30°C was obtained; the same value (12 m<sup>2</sup>/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.

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

Such a phenomenon can be described as follows: adsorption is an exothermic process [66; and according to the principle of Le Chatelier and the rule of Van't Hoff: the effect of a change in temperature on a system at equilibrium is to shift the equilibrium in the direction that acts to counteract and nullify the temperature change. This means increasing temperature hinders adsorption and promotes desorption; as a consequence a lesser number of molecules can be adsorbed. This phenomenon is very well-known in adsorption science. Many studies can be found in the literature which show the impact of temperature on sorption isotherms for different adsorbents and adsorbates [50; 68-73], the results always show the same modifications of the sorption isotherms as described in this paper. Furthermore in adsorption technology, the temperature increase and the heat transfers induced by the heat of adsorption are accounted for the design of the adsorbent beds (to avoid the performance reduction due to temperature increase) and thermal treatments at elevated temperature are usually used as a method to regenerate adsorbents (this method is also know as "temperature swing adsorption") [73; 74].

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

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

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

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

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

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

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





Fig. 9. Comparison between the isosteric heat of desorption obtained in this study (two
isotherms at two different temperatures and Clausius-Clapeyron) and the one proposed by
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℃ to 80℃. 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

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 pronounced396 non-linearities;
- 397 2. the water content at equilibrium is drastically reduced at 80℃ over the whole RH
  398 range;
- 399
  - 3. the water content at saturation at  $80^{\circ}$  is significantly lower than at  $30^{\circ}$ .

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 compare it to the data obtained by Powers & Brownyard using a different method at constant 405 406 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.)

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### 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,
- Institut National Polytechnique de Grenoble (INPG), 1986, 319p.p.
  J.-F. Daïan, Condensation and isothermal water transfer in cement mortar, part I pore size distribution, equilibrium, water condensation and imbibition, Transport in
  Porous Media 3(6) (1988) 563-589.
- F. Radjy, E.J. Sellevold, K.K. Hansen, Isosteric vapor pressure-temperature data for
  water sorption in hardened cement paste: enthalpy, entropy and sorption isotherms at
  different temperatures, Report BYG-DTU R057, Technical University of Denmark
  (DTU), Lyngby, Denmark, 2003, 58p.

432 433	[6]	T. Ishida, K. Maekawa, T. Kishi, Enhanced modeling of moisture equilibrium and 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 zemestein, zementmörtel und
436	r. 1	beton (in german). Deutscher Ausschuss für Stahlbeton Heft 297 (1978) 25-39.
437	[8]	7 P. Bažant W. Thonguthai. Pore pressure and drving of concrete at high
438	[0]	temperature Journal of the Engineering Mechanics Division (ASCE) 104(5) (1978)
439		
440	[9]	7 P. Bažant, J.C. Chern, W. Thonguthai, Finite element program for moisture and
441	[0]	heat transfer in heated concrete. Nuclear Engineering & Design 68(1) (1980) 61-70
1/12	[10]	7 P. Bažant W. Thonguthai. Pore pressure in heated concrete walls - theoretical
1/2	[IU]	prediction Magazine of Concrete Research 31(107) (1070) 67-76
443	[11]	B Bary A polydisported particle system representation of the poresity for pop-
444	[ ' ' ]	b. Daily, A polydispersed particle system representation of the polosity for hore-
445		
440	[4:0]	2001.
447	[12]	L.J. Killikenberg, The permeability of porous media to liquid and gases, American
448	[40]	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 Committe 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. Radiv, 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	[י ב]	materials Cement and Concrete Research 35(12) (2005) 2271-2277
475	[22]	R S Mikhail G A Oweimreen Surface area and nore structure of compressed low-
476	[בכ]	norosity compute pastes. Compute and Concrete Research 3/5) (1973) 561-573
470	[23]	CEN Tosting bardonod concrete, part I: shape, dimensions and other requirements
470	[23]	for test specimens and moulds. European Committee for Standardization. European
470		Standard EN 12200 1 (2001) 10p
479	[24]	L Booudouin BT Tomtoio Effort of druing mothods on microstructural changes in
400	[24]	J.J. Deaudouili, B.T. Tallisia, Effect of drying methods of microsifuctural changes in
401 400		Advanced Concrete Technology 2(1) (2004) 442 420
40Z	[05]	Auvanueu Cunulete Teunnuluyy 2(1) (2004) 113-120.
403 404	[2ວ]	o. Gaile, Effect of drying on cement-based materials pore structure as identified by
484		freeze drying Comparison porosimetry. A comparative study between oven-, vacuum-, and
480		neeze-orying, Cement and Concrete Research 31(10) (2001) 1467-1477.

486 G.G. Litvan, Variability of the nitrogen surface area of hydrated cement paste, [26] 487 Cement and Concrete Research 6(1) (1976) 139-144. 488 J.J. Beaudouin, J. Marchand, Pore structure, in: V.S. Ramachandran and J.J. [27] 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. A. Korpa, R. Trettin, The influence of different drying methods on cement paste 494 [29] 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 I. Pane, W. Hansen, Surface characteriation of blended cements by H<sub>2</sub>O and N<sub>2</sub> [31] sorption isotherms, in: J. Weiss, K. Kovler, J. Marchand and S. Mindess (Eds), 503 Proceedings of the the 1<sup>st</sup> International Symposium on Advances in Concrete through 504 505 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℃, 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. Černy, 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 S.F. Wong, T.H. Wee, S. Swaddiwudhipong, S.L. Lee, Study of water movement in [35] 516 concrete, Magazine of Concrete Research 53(3) (2001) 205-220. 517 T.C. Powers, H.M. Mann, L.E. Copeland, The flow of water in hardened Portland [36] 518 cement paste, Portland Cement Association Bulletin 106 (1959) 18p. R.B. Anderson, Modifications of the Brunauer, Emmett and Teller equation, Journal of 519 [37] 520 the American Chemical Society 68(4) (1946) 686-691. 521 C. van der Berg, Vapour sorption equilibria and other water-starch interactions: a [38] 522 physico-chemical approach, Ph-D thesis, Agricultural University of Wageningen, The 523 Netherlands, 1981, 186p. S. Brunauer, J. Skalny, E.E. Bodor, Adsorption on non porous solids, Journal of 524 [39] 525 Colloid and Interface Science 30(4) (1969) 546-552. P.-N.T. Johnson, J.G. Brennan, Moisture sorption isotherm characteristics of plantain 526 [40] 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. Jonquières, 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. [44] Y. Xi, Z.P. Bažant, H.M. Jennings, Moisture diffusion in cementitious materials -536 537 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 S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, [47] 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 J.B. Condon, Surface area and porosity determinations by physisorption -[49] 550 Measurements & theory, Elsevier, 2006, 274p. S.J. Gregg, K.S.W. Sing, Adsorption, surface area and porosity, Academic Press. 551 [50] 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 as measured by various techniques, Concrete Science and Engineering 1(1) (1999) 559 560 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 analysis by water vapor adsorption. III. Analysis of hydrated calcium silicates and 567 568 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℃, 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 P.C. Carman, F.A. Raal, Physical adsorption of gases on porous solids I -[62] 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, Mathematical and Physical Sciences 209(1096) (1951) 69-81. 587 588 [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, Massachussets, USA, 2005, 422p.
- 599 [69] A.A. Fomkin, Adsorption of gases, vapors and liquids by microporous adsorbents,
   600 Adsorption 11(3) (2005) 425-436.
- [70] I.I. Salame, T.J. Bandosz, Experimental study of water adsorption on activated
   carbons, Langmuir 15(2) (1999) 587-593.
- [71] I.I. Salame, T.J. Bandosz, Adsorption of water and methanol on micro- and
   mesoporous wood-based activated carbons, Langmuir 16(12) (2000) 5435-5440.
- [72] D.D. Do, Adsorption analysis: equilibria and kinetics, Series on Chemical Engineering
   Vol. 2, Imperial College Press, London, United Kingdom, 1998, 913p.
- R.T. Yang, Adsorbents: fundamentals and applications, John Wiley and Sons,
  Hoboken, New Jersey, USA, 2003, 425p.
- 609 [74] M. Suzuki, Adsorption engineering, Elsevier Science, Amsterdam, The Netherlands, 610 1990, 270p.
- 611 612