

1 A study of the water vapor sorption isotherms of hardened
2 cement pastes: possible pore structure changes at low relative
3 humidity and the impact of temperature on isotherms

4 Min Wu^a, Björn Johannesson^a, Mette Geiker^b

5 *a. Department of Civil Engineering, Building 118, Technical University of Denmark, 2800 Lyngby,*
6 *Denmark*

7 *b. Department of Structural Engineering, Norwegian University of Science and Technology,*
8 *Trondheim, Norway*

9 **Abstract**

Using water vapor sorption isotherms measured by the “dynamic vapor sorption” (DVS) method, a resaturation study was conducted to investigate possible pore structure changes of hardened cement paste samples caused by the drying at low relative humidity during desorption measurements. The results indicate that either the relatively short term drying does not cause any microstructure changes or the pore structure of the hardened cement paste samples can be restored during the absorption process. Additionally, the temperature dependency of sorption isotherms was investigated using both hardened cement paste samples and a model material MCM-41. The pronounced impact of temperature on desorption isotherms of cement based materials as reported in literature was not found in this investigation. The results suggest that the differences between the sorption isotherms measured at different temperatures are mainly caused by the temperature dependent properties of water.

10 *Keywords:* Adsorption (C); cement paste (D); microstructure (B); temperature (A);
11 isotherms.

1. Introduction

Water vapor sorption isotherms of a porous material are the graphic representation of the water content against the relative humidity (RH) of the environment at equilibrium condition, i.e., the RH inside of the material is equal to that of the external. Based on the determined water vapor isotherms, it is possible to derive important properties of the material under study. For hardened cement pastes, the properties including, e.g., the bulk porosity accessible to water vapor, the porosity and the amount of the hydration products-calcium silicate hydrate (C-S-H) gel, the specific surface area, the pore size distribution as well as the connectivity of the pores, can be studied [1, 2]. Moreover, the transport properties, such as the permeability and the diffusion coefficients of the hardened paste can also be obtained from studying the sorption isotherms [3]. Additionally, the derived properties from the water vapor sorption isotherms are quite essential in the modeling of some important processes, e.g., moisture transport [3, 4], drying shrinkage [5] and carbonation [6, 7]. A clarification is made here about the terminology “adsorption” and “absorption”. In many cases, e.g., see [8], “adsorption” is used in describing the process of the liquid uptake, including both the adsorbed and the capillary condensed liquid. While some other authors, e.g., see [9, 10], use “absorption” to describe exactly the same content, i.e., including both types of liquid uptake. In this work, the word “absorption” will be used to describe the combined effect of both the adsorption and the capillary condensation while “adsorption” simply refers to the liquid fixed due to multilayer adsorption.

It has been reported in some studies, e.g., see [1, 11–15], that changes of the pore structure of hardened cement paste samples can be expected during desorption measurements when the RH decreases to low values, e.g., below the RH of about 0.4. It

36 has been argued by Jennings et al. [12–14] that drying below the RH at about 0.4
37 results into the restructure, or more precisely the collapse of the low density (LD) C-
38 S-H products. Additionally, it is argued in [12–14] that the loose-packed C-S-H will be
39 converted into LD C-S-H at very low RHs. Based on a colloid description of the C-S-H
40 structure, an explanation was proposed by the same authors, which is that the drying
41 enhances the chemical aging, i.e., the increase of the polymerization degree of the sil-
42 icate chains in the C-S-H particles over time. This kind of irreversible chemical aging
43 will change the C-S-H particles into stiffer, stronger and denser ones. Baroghel-Bouny
44 [1] studied the first and second desorption isotherms of several different hardened ce-
45 ment paste samples and concluded that microstructure changes occurred in some of
46 the studied samples, represented by higher water contents measured during the second
47 desorption isotherm in the low RH range (especially for RH between 0.33-0.12). Some
48 other studies, e.g., in [11], reported that the pore structure of hardened cement paste
49 samples was coarsened by the so-called drying effect at low RHs. Thus, it should be
50 mentioned that for the same behavior of pore structure changes in this context, con-
51 tradictory results have been reported, e.g., the results in [1] demonstrate the increase
52 of small pores while that in [11] indicate the coarsening of the pore structure. Due
53 to the instability caused by the drying involved in the desorption process, the first
54 and the second desorption isotherm cycles have been studied rather extensively. It has
55 been suggested that the second desorption is more stable and thus it should be more
56 representative for a pore structure analysis [15]. However, based on some experimen-
57 tal evidence, Baroghel-Bouny [1] also pointed out that the microstructure changes of
58 cement pastes caused by the drying at low RHs are reversible, which is different from
59 the permanent changes as reported and discussed by Jennings et al. [12–14].

60 The influence of temperature on the sorption isotherms of cement based materi-
61 als has been reported, e.g., in [16–21]. The absorption isotherms measured by Daian
62 [19] between 20 °C and 55 °C demonstrated that the higher the temperature, the less
63 the amount of the absorbed water at a certain RH. However, the differences between
64 the absorption isotherms measured under different temperatures were rather small.
65 Similar results were also reported in the study conducted by Radjy et al. [20]. The
66 authors measured the absorption isotherms between 0 °C and 60 °C and the desorption
67 isotherms between 0 °C and 40 °C on mature hardened cement paste samples, and the
68 results showed hardly any temperature dependent property. Ishida et al. [21] inves-
69 tigated the absorption and desorption isotherms for a 80-day water cured hardened
70 cement paste samples under 20 °C, 40 °C and 60 °C. Very limited differences were
71 found in the absorption isotherms in that study, however, the differences in the des-
72 orption isotherms were found to be more pronounced. As the temperature increases,
73 not only the amount of water adsorbed decreased but the shape of the isotherms was
74 also concluded to be modified [21]. Similar behavior, i.e., rather significant differences
75 of the desorption isotherms under different temperatures, was reported in [16–18]. The
76 temperature dependence of sorption isotherms of cement based materials can be at-
77 tributed to two different mechanisms [22, 23]: (1) the coarsening of pore structure,
78 e.g., ettringite dissolution and C–S–H alteration; and (2) the temperature dependence
79 of water properties. Poyet et al. [16, 17] pointed out that yet another factor may be
80 involved in influencing the sorption isotherms at different temperatures. They assumed
81 that the isotherm evolution is purely due to the so-called “thermal desorption”, which
82 is to say that the shift of the adsorbed water content on the desorption isotherms at
83 different temperatures is induced only by the temperature effect while the potential

84 microstructure changes are considered as negligible. Based on these assumptions and
85 the Clausius-Clapeyron formula, they developed a method to predict the desorption
86 isotherms under different temperatures using a desorption isotherm measured at one
87 temperature as a reference state. If the rather pronounced differences between des-
88 orption isotherms measured at different temperatures are due to the thermal effect as
89 argued by, e.g., Poyet et al. [16, 17], similar differences should be observed also on
90 absorption curves measured at different temperatures while little difference is reported
91 [16, 17]. Since the reported results regarding the temperature dependent isotherms are
92 not consistent for cement based materials, further exploration in this aspect is needed.

93 In the present work, possible changes of the pore structure of hardened cement paste
94 samples at low RHs will be investigated through a resaturation method. Following a
95 first desorption-absorption cycle, where the desorption goes down to $RH = 0$, the
96 tested samples will be resaturated with distilled water. After that, a second desorption-
97 absorption cycle will be conducted on the resaturated samples. In this way, the changes
98 of the pore structure of the studied hardened cement paste samples at low RHs are
99 expected to be observed by comparing the sorption isotherms of the first and the second
100 cycle, if there is any. Moreover, the sorption isotherms will be measured under different
101 temperatures to study important influencing factors with respect to the temperature
102 dependence of the sorption isotherms of hardened cement pastes.

103 **2. Experimental**

104 *2.1. Materials preparation*

105 Three materials were studied in this investigation: one model porous material named
106 MCM-41 and hardened cement pastes prepared by two types of cement. By including
107 the model material MCM-41, whose pore structure is considered stable during the

Table 1: Properties and the chemical composition of the two cements used in this study.

		CEM I (CEM I 32.5 R)	CEM III (CEM III/B 42.5 N)
Density	(g/cm ³)	3.06	2.90
Fineness	(cm ² /g)	2905	4635
Water demand	(%)	26.2	32.3
Initial setting time	(min)	185	270
Loss on ignition	(%)	2.1	1.4
SiO ₂	(%)	20.6	29.2
Al ₂ O ₃	(%)	5.6	8.9
Fe ₂ O ₃	(%)	2.4	1.2
CaO	(%)	63.4	48.0
MgO	(%)	1.6	4.8
SO ₃	(%)	2.9	2.6
K ₂ O	(%)	0.7	0.6
Na ₂ O	(%)	0.2	0.2
Cl	(%)	<0.1	<0.1

108 studied temperature range (25-40 °C), it can provide reference information in the study
 109 of the temperature dependent isotherms in which the factor of the changing of pore
 110 structure caused by temperature can be excluded.

111 MCM-41 is a silica based material whose pore structure is in the form of hexagonal
 112 arrays of uniform tubular channels of controlled width, which is often used as a model
 113 material in porosity studies. The MCM-41 used in this study is produced by Tianjin
 114 Chemist Scientific Ltd. The information provided by the producer concerning the pore
 115 diameter, the specific surface area and the total pore volume is 3.0 nm, ≥ 800 m²/g
 116 and ≥ 0.70 ml/g, respectively.

117 CEM I 32.5 R and CEM III/B 42.5 N were the two types of cement used to prepare
 118 the paste samples, see Table 1. The W/C ratio for all cement paste samples was
 119 0.4. The paste samples were mixed using a paddle mixer. After mixing, the pastes

120 were cast into plastic vials with a diameter of about 15 mm and a length of about
121 50 mm followed by proper compaction. After the sealed curing at room temperature
122 (about 20 °C) in the plastic vials for about one day, the hardened paste samples were
123 demoulded. Then, each paste sample was placed into a slightly bigger plastic flask
124 filled with saturated limewater to cure at room temperature until the desired age for
125 experiments was reached. In the following description, the hardened cement pastes will
126 be denoted as CEM I and CEM III.

127 The cement paste samples were cured for about 6 months before testing. Before
128 sorption measurements, the prepared cylinder samples of the hardened cement pastes
129 were vacuum saturated with saturated limewater and then the crushing and grinding
130 of the samples was conducted in a carbon dioxide free chamber since very small sample
131 size was needed (section 2.2). To avoid possible drying during the process, the RH
132 inside of the chamber was set at 1 (the measured RH was about 0.90-0.95) and the
133 sample crushing and grinding was conducted rather quickly (in 30-40 minutes) for
134 each paste. Immediately after that, the ground powder was placed into plastic flasks
135 containing saturated limewater with the amount just to cover the powders (for about a
136 week) before the sorption experiments. This procedure was also conducted in a carbon
137 dioxide free chamber.

138 One concern with respect to the sample preparation of cement pastes is that the
139 powder samples might not be fully saturated by submerging in limewater, even though a
140 vacuum saturation was performed before the sample crushing. To check the saturation
141 situation, powder samples were subjected to reduced pressure (~ 40 mbar) for about 3
142 hours followed by 24 hours of standing still. After that, the total (lime)water contents
143 were determined. Compared with the samples submerged in limewater, the relative

144 difference of the total (lime)water content was less than about 5%. In this sense, we
145 think it is acceptable to submerge the powder samples in limewater for the purpose of
146 sorption measurements.

147 Another concern is that drying might have already taken place during the sample
148 preparation of cement pastes, even if special care was taken. To see the extend of water
149 loss during the sample crushing, the desorption curve of a powder sample of CEM I
150 paste measured by the DVS instrument was checked. It is because the first step of the
151 desorption measurement (with RH set at 0.95) can be approximated to what takes place
152 during the sample crushing in the carbon dioxide free chamber. The initial mass of
153 the sample (after taking out from the sample vial covered by limewater, which includes
154 some bulk water adhered to the sample surface) was about 16 mg; the dry mass later
155 determined at $\text{RH} = 0$ was about 8 mg and the water loss during the first half hour of
156 the measurement was about 1 mg. That is, during the first half hour, most of the water
157 lost is the bulk water adhered to the sample surface (since the total pore water later
158 determined at the $\text{RH} = 0.95$ from the desorption was about 21% of the dry mass, i.e.,
159 about 1.6 mg). In this sense, the drying effect during sample crushing is considered
160 limited.

161 More importantly, as will be shown later, some arguments of this study are mainly
162 drawn based on the comparison of the results obtained by the DVS method and that
163 by the traditional desiccator method using salt solutions. It often takes long time, e.g.,
164 several weeks to months, to measure a sorption data at one RH using the desiccator
165 method [11, 12, 15]. That is, the drying effect of the samples using desiccator method
166 should be much more pronounced compared with that in the DVS method used here.
167 If the desiccator method can catch the first sorption isotherms (which is often assumed

168 so in literature, e.g., see [1]), it is then reasonable to think that the DVS method for
169 sure can also catch the first sorption isotherms.

170 *2.2. Sorption measurements*

171 The “dynamic vapor sorption” (DVS) method was used to measure the sorption
172 behaviors of the materials in this investigation. The sorption measurements were con-
173 ducted in a climate incubator in which the temperature can be accurately regulated
174 and controlled. The desired relative humidity can be generated by mixing two air flows,
175 i.e., a totally dry (RH = 0) and a totally saturated (RH = 1) air in various proportions.
176 The proportion of the two flows is controlled by the input settings of the instrument.
177 Figure 1 is a schematic illustration of a DVS instrument. More detailed descriptions of
178 the instrument can be found in [24].

179 It should be noted that it can take very long time for the equilibrium condition to be
180 established at a given pre-set relative humidity. Consequently, it is almost practically
181 impossible to wait for the establishment of the equilibrium condition at each relative
182 humidity in a sorption measurement. The duration time of each relative humidity in
183 the DVS instrument can be controlled by either setting the mass change ratio against
184 time, dm/dt , or by setting the duration time directly. Once the set conditions are
185 met, the instrument will directly go to the next step of the pre-set relative humidities.
186 In this study, the dm/dt criterion is set to 0.002% and the shortest and the longest
187 duration time for each RH step is set to be 0.5 and 24 hours, respectively. Then, the
188 equilibrium moisture content corresponding to each generated relative humidity step
189 will be extrapolated from the measured data. The details about the extrapolation will
190 be presented later. The temperature of the measurements was 25 °C except when it is
191 specifically stated.

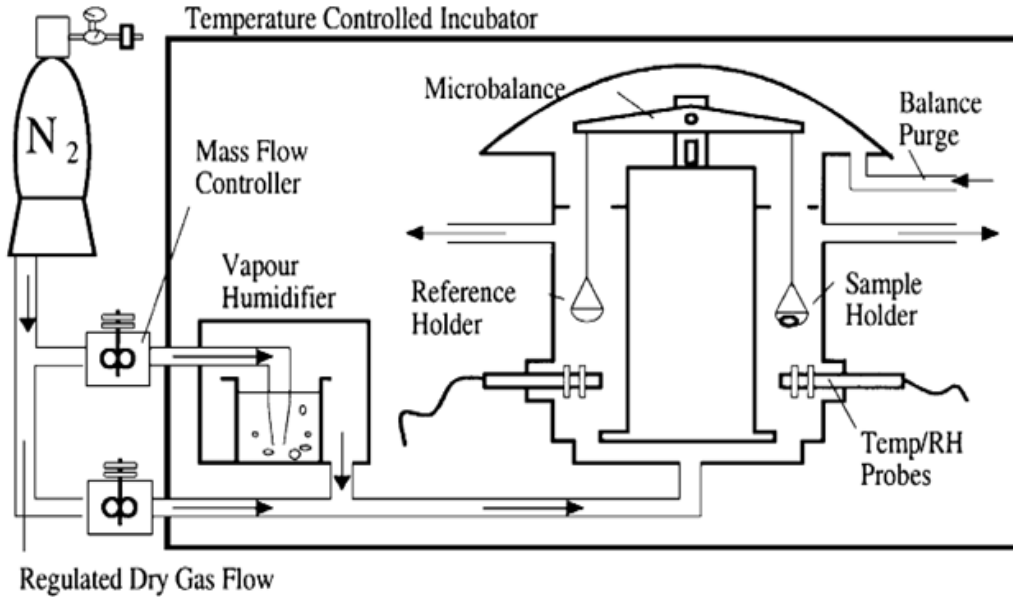


Figure 1: Schematic illustration of a dynamic vapor sorption (DVS) instrument. Dry and saturated air are mixed to generate the desired relative humidity and a symmetric reference holder is used to counteract the adsorption on the sample holder (after [24]).

192 The sorption measurement for the model material MCM-41 started from an absorp-
 193 tion (RH from 0 to 0.95) followed by a desorption (RH from 0.95 to 0) measurement.
 194 Considering the possible effect of drying at low RHs on the microstructure as discussed
 195 earlier, the experiments with hardened cement paste samples started from the desorp-
 196 tion and then followed by the absorption. By adopting this procedure, the possible
 197 effect caused by the so-called drying damage at low RHs is expected to be reduced.

198 For each material under study, sorption measurements were conducted three times
 199 using different samples. The total sorption experimental study lasted for about four
 200 months and the three sets of measurements were undertaken at the beginning, the
 201 middle and the end of the total measuring time. By doing this, firstly the stability
 202 of the instrument can be validated as the model material MCM-41 has a stable pore

203 structure which will not change against time; and secondly the possible evolution of
204 the pore structure against time of the hardened cement paste samples can be checked
205 since further hydration might take place in cement based materials even though some
206 relatively mature samples are used.

207 Concerning the resaturation study of the two hardened cement pastes, firstly a
208 desorption-absorption cycle was conducted. After this cycle, each tested sample was
209 resaturated with distilled water for about 3 days. The resaturation was conducted
210 by adding several drops of distilled water on each of the tested sample in the sample
211 holder (see Figure 1). After the resaturation, a second desorption-absorption cycle was
212 applied on the samples. Immediately after the second desorption-absorption cycle, a
213 scanning desorption curve starting from $RH = 0.95$ to $RH = 0$ was measured on each
214 sample.

215 **3. Results and discussion**

216 *3.1. Instrument and sample stability*

217 The results of the three sorption measurements for the model material MCM-41
218 are presented in Figure 2. Generally, the measured results on the three samples are
219 rather comparable, especially on the desorption isotherms. If we compare the three
220 desorption measurements in RHs lower than about 0.45, they are observed to be almost
221 identical. For the point at $RH = 0.5$, the small difference observed might be related to
222 the homogeneity of the sample since very small sample (less than 10 mg in this case)
223 was used. Another possible reason for the differences might be due to the instrument
224 setting with regard to the equilibrium condition. It can be found in Figure 2 that the
225 major desorption occurs between the RH of 0.45 to 0.55. That is, there is a possibility
226 that the equilibrium condition was not established at $RH = 0.5$ during the pre-set

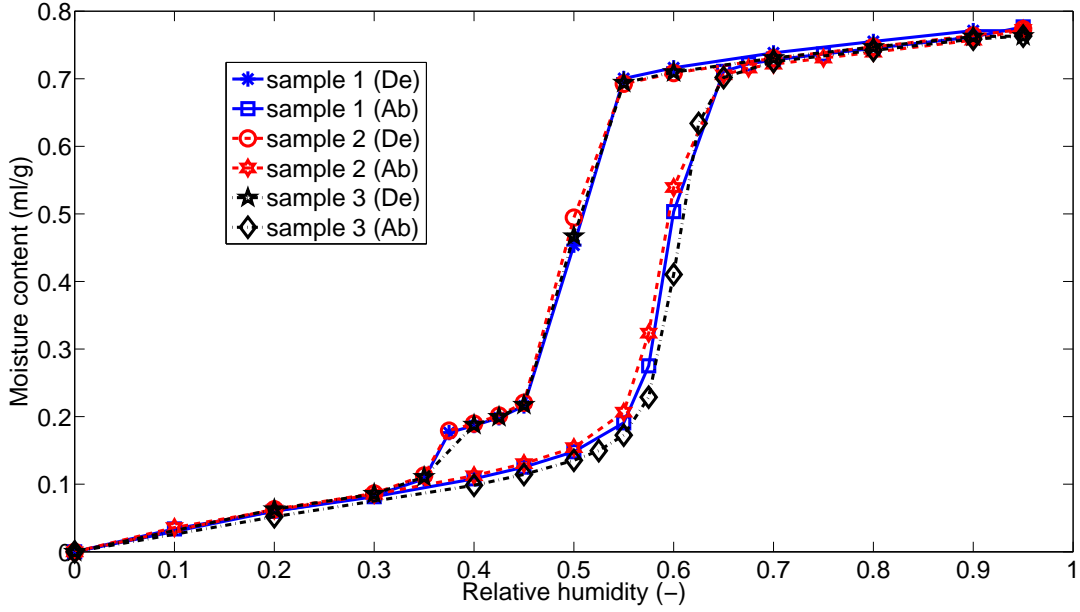


Figure 2: Three sorption measurements for the model material MCM-41. “De” and “Ab” denote desorption and absorption, respectively. The moisture content is expressed as ml water per gram of dry sample and the mass of the dry sample is determined at the point where $RH = 0$.

227 duration time of each RH step (24 hours), e.g., see the desorption isotherm of sample
 228 2, which shows a slightly higher value than other measurements. The similar trend
 229 of non-equilibrium as observed in the desorption isotherms can also be found in the
 230 absorption curves. Concerning the absorption isotherms, the agreement is, however,
 231 quite satisfactory both at high (> 0.7) and low RH (< 0.4) ranges with differences
 232 found only at the middle RH range (0.4-0.7). The same arguments as presented for the
 233 desorption isotherms are also applicable for the absorption isotherms.

234 The measured sorption isotherms for the two hardened cement pastes CEM I and
 235 CEM III are shown in Figure 3 and Figure 4. As can be observed, a fairly good
 236 comparability is found in the absorption isotherms for both CEM I and CEM III in
 237 the whole RH range while there are some differences in the desorption isotherms. The

238 differences in CEM I (Figure 3) lie in high RHs and $RH < 0.4$ while the differences in
239 CEM III (Figure 4) are mainly at high RHs (0.8-0.95). The differences measured at
240 the high RHs can be attributed to that the equilibrium condition is not established,
241 which is similar to what has been discussed for the MCM-41 in the same context
242 but with some additional differences. Here, however, the main reason causing the
243 equilibrium condition not being achieved is due to the adopted experimental procedure.
244 As mentioned earlier, in order to avoid any possible carbonation and pre-drying, the
245 cement paste samples need to be cured in saturated limewater before the desorption
246 measurement started. That is, there was some surplus water adhered to the outer
247 surfaces of the hardened cement pastes. This water might not be able to be desorbed
248 during the pre-defined 24 hours for each step at the very high RHs. This is especially
249 true for the first step of a desorption, i.e., at $RH = 0.95$. The original measured data
250 confirmed the relevance of the above mentioned argument, i.e., the dm/dt was still
251 higher than the pre-set value at some of the high RH points shown in Figure 3 and
252 Figure 4 when it went to the next RH step. As will be presented later, a procedure will
253 be introduced to extrapolate the sample mass under equilibrium conditions. The main
254 differences between a measured isotherm and the corresponding corrected isotherm
255 (with the extrapolated data) are at very high RHs. That is, most of the differences at
256 the high RHs will be canceled out by adopting the proposed extrapolation procedure.

257 By looking at the data measured for CEM I at $RH < 0.4$ (Figure 3), the desorption of
258 measurement 1 shows higher moisture content than that of sample 2 and sample 3 while
259 the desorption isotherms of sample 2 and sample 3 are almost identical in the considered
260 RH range. It may be suspected that it is the continuing hydration process which has
261 altered the porosity of the material. However, it should be noticed that firstly the total

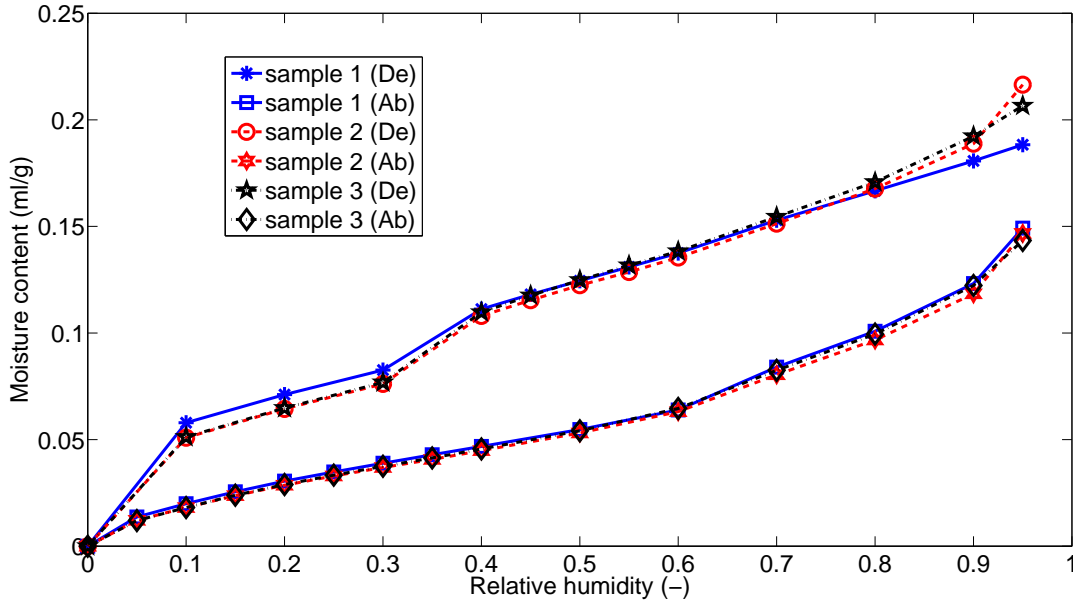


Figure 3: Three sorption measurements for the hardened cement paste CEM I. “De” and “Ab” denote desorption and absorption, respectively. The moisture content is expressed as ml water per gram of dry sample and the mass of the dry sample is determined at the point where $RH = 0$.

262 porosity (demonstrated by the maximum moisture content) of sample 2 and sample 3
 263 are not reduced; and secondly the difference is not found for sample CEM III (Figure
 264 4). Compared with CEM I, CEM III includes much more supplementary cementitious
 265 component (ground granulated blast furnace slag). That is, the continuing hydration
 266 would be more likely in sample CEM III than in CEM I given the same hydration age
 267 while this is not the case in this study. Additionally, the same type of difference is
 268 not observable in the measured absorption isotherms. Therefore, it is assumed that
 269 the samples used are old enough and that the change of the pore structure due to
 270 further hydration during the measurement period is presumably low. The relatively
 271 small difference observed at $RH < 0.4$ for CEM I comparing the three measurements
 272 might instead be related to some unknown uncertainties during the the desorption

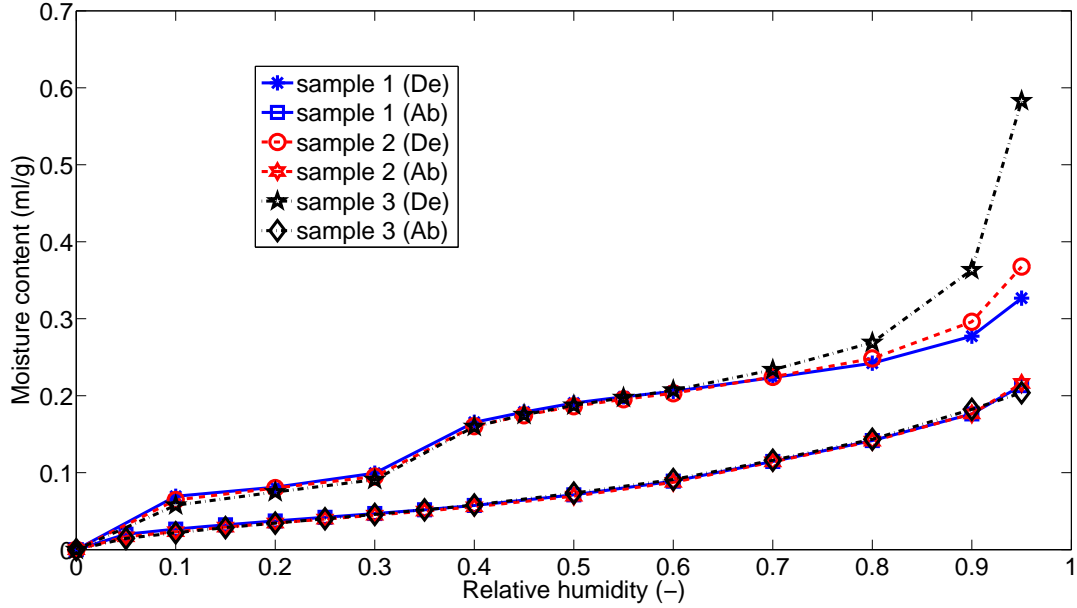


Figure 4: Three sorption measurements for the hardened cement paste CEM III. “De” and “Ab” denote desorption and absorption, respectively. The moisture content is expressed as ml water per gram of dry sample and the mass of the dry sample is determined at the point where RH = 0.

273 measurement of sample 1.

274 3.2. Extrapolation of sorption data

275 As mentioned in subsection 2.2, it is almost practically impossible to wait for the
 276 establishment of equilibrium condition at each studied RH step. Therefore, a data
 277 processing procedure (curve fitting) is adopted to extrapolate the sample mass to its
 278 equilibrium condition. It has been proposed that the sample mass against time in a
 279 sorption measurement follows the equation [25, 26]

$$m(t) = m_f - (m_f - m_0)e^{-k(t-t_0)} \quad (1)$$

280 where $m(t)$ is the sample mass at the time t , m_0 is the initial mass and t_0 is the initial
 281 time of the curving fitting, m_f is the fitted asymptotic sample mass at the equilibrium

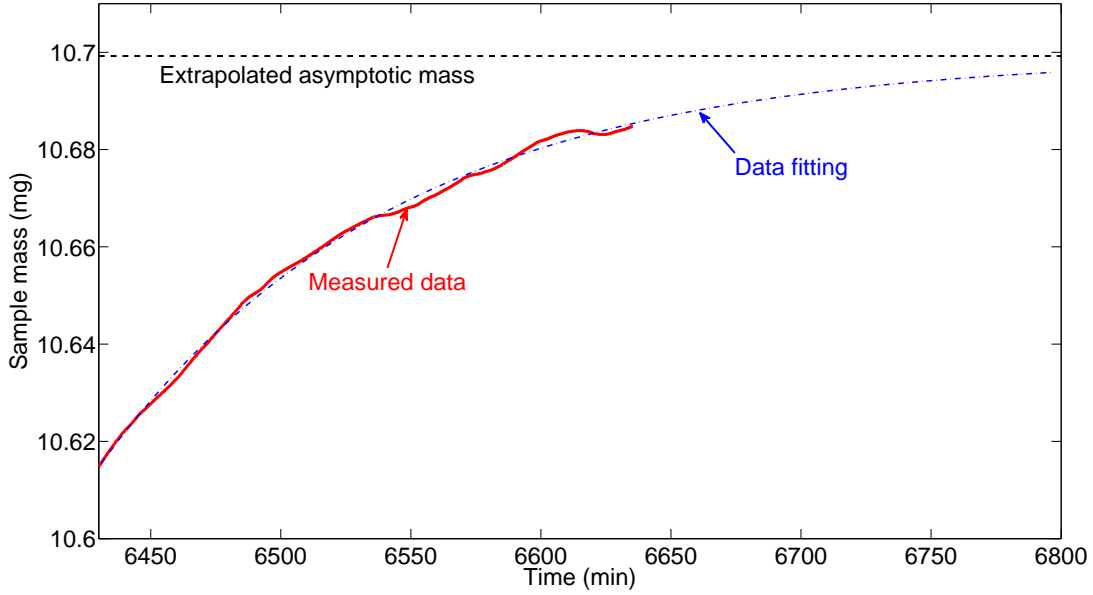


Figure 5: An example showing the data processing procedure to extrapolate the asymptotic sample mass at the equilibrium conditions.

282 condition for the studied RH and k is a curve fitting constant. Figure 5 gives an
 283 illustration of a data extrapolation. The solid line is the measured experimental data;
 284 the dash-dot line represents the fitted curve and the dot line shows the extrapolated
 285 asymptotic sample mass at the assumed equilibrium condition for the considered RH
 286 step.

287 Using the extrapolated data, the corrected isotherms under the assumed equilibrium
 288 conditions can be plotted. For the model material MCM-41(besides the point at RH
 289 = 0), the point with important difference between the extrapolated and the measured
 290 isotherms is found at RH = 0.5 in desorption and at a RH around 0.6 in absorption in
 291 which moisture desorbs/condenses rather drastically. For the studied hardened cement
 292 pastes CEM I and CEM III, the point at RH = 0 is a point with relatively big difference
 293 between the extrapolated and the measured isotherms, which indeed is similar to the

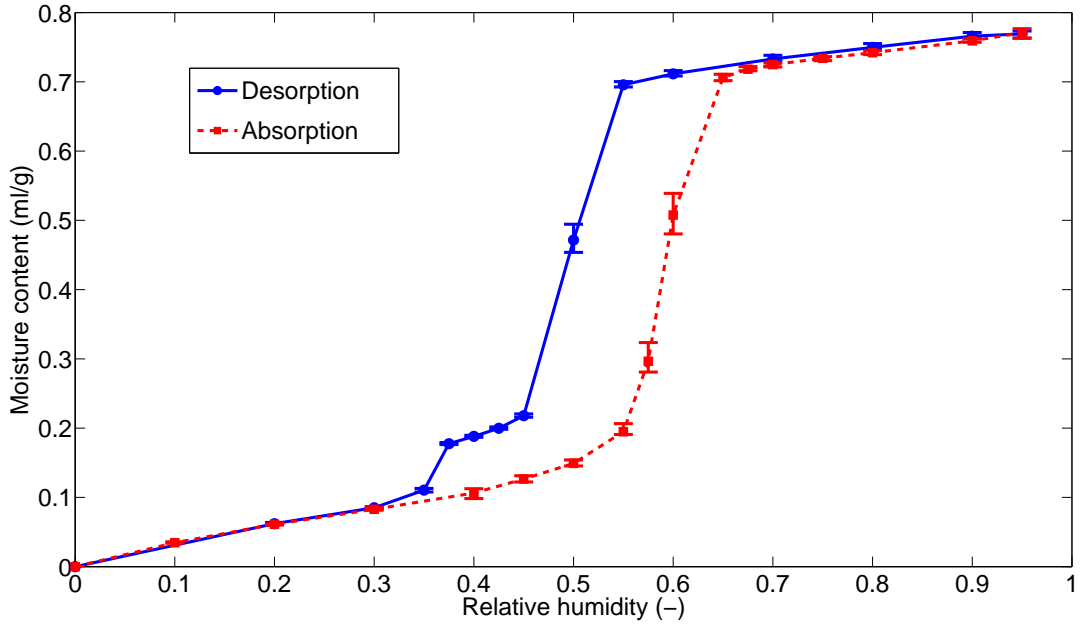


Figure 6: The sorption isotherms for MCM-41 based on the extrapolated data. The error bar shows the variation of three repetitive measurements as presented earlier.

294 results of the MCM-41. However, more points with important difference are found
 295 at the high RHs (0.95, 0.9 and sometimes 0.8) of the studied hardened cement paste
 296 samples, especially between the extrapolated and the measured desorption isotherms.
 297 The reason has been discussed already, i.e., related to the experimental procedure and
 298 the pre-setting in the instrument. For other RH points than the ones discussed above,
 299 the relative difference of the moisture content between the extrapolated and measured
 300 data are no more than about 0.3%.

301 With the extrapolated data, the corrected sorption isotherms of the three studied
 302 materials were constructed and they are presented in Figure 6, Figure 7 and Figure 8.

303 3.3. Resaturation of hardened cement paste samples

304 Considering the comparable results obtained on different samples in the sorption
 305 measurements as discussed in subsection 3.1, each measurement for the resaturation

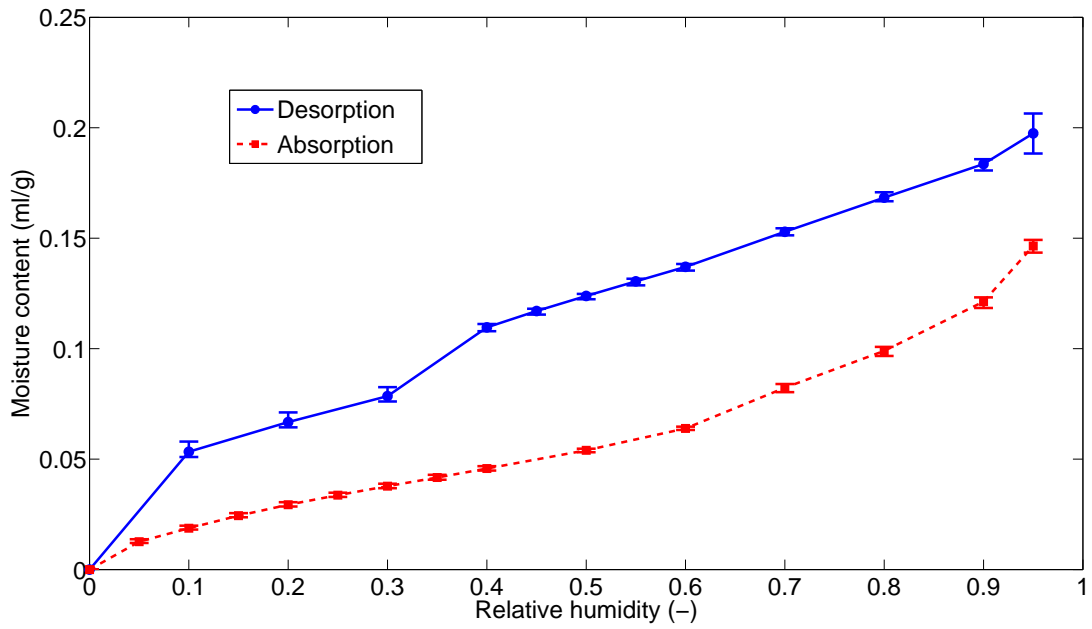


Figure 7: The sorption isotherms for CEM I based on the extrapolated data. The error bar shows the variation of three repetitive measurements as presented earlier.

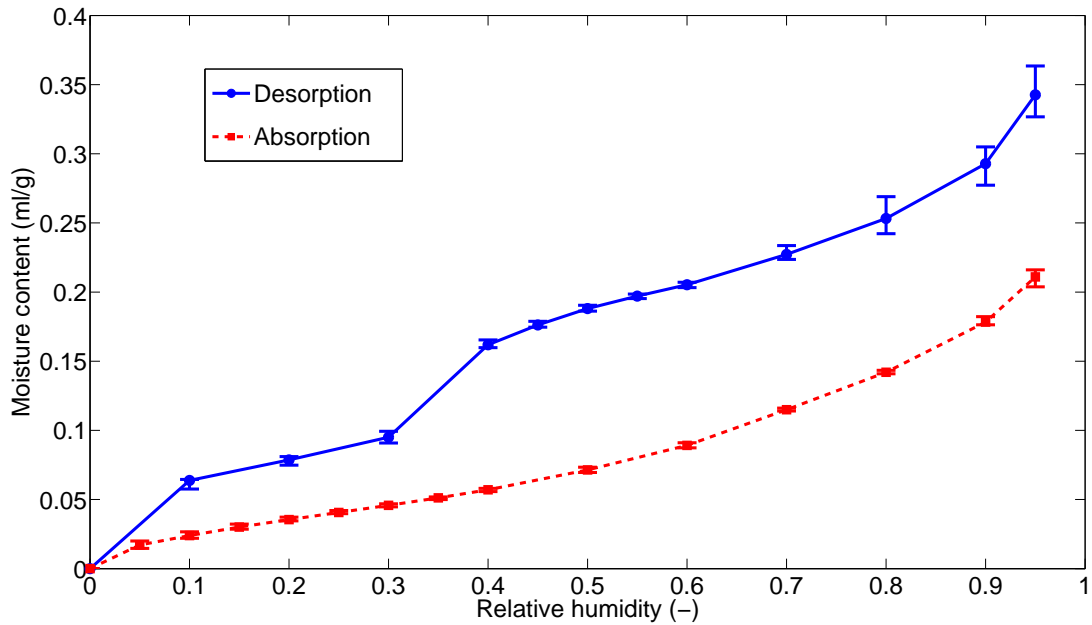


Figure 8: The sorption isotherms for CEM III based on the extrapolated data. The error bar shows the variation of three repetitive measurements as presented earlier.

306 study was conducted only once. The sorption isotherms (after data extrapolation to
307 equilibrium) are shown in Figure 9 and Figure 10. It can be observed that there is
308 actually no major difference between the first absorption isotherm (denoted as the
309 “original” isotherm) and the second after resaturation (denoted as the “resaturated”
310 isotherm) for both cement pastes the CEM I and CEM III. Comparing the first desorp-
311 tion isotherm with the one after resaturation, one can conclude that they follow about
312 the same path but the isotherm after resaturation is slightly lower than the original
313 one. The difference between the two desorption isotherms becomes smaller as the RH
314 decreases. It would be reasonable to argue that the difference in the measured response
315 is due to the fact that the adopted resaturation procedure cannot fully saturate all of
316 the pores, especially the big pores, rather than the change of the pore structure. The
317 relevance of this argument can be motivated by looking at the desorption scanning
318 curve started from the point $RH = 0.95$ following the absorption measurement of the
319 resaturated sample. The difference between the original desorption isotherm and the
320 scanning curve also follows about the similar trend as observed for that between the
321 original desorption isotherm and the isotherm after the resaturation, but the difference
322 is much bigger, especially at high RHs. This is reasonable because for the scanning
323 curve, the pores whose Kelvin radii are larger than that corresponding to the RH of
324 0.95 are empty when the desorption starts. While for the original desorption at $RH =$
325 0.95, these pores with pore entry radii (Kelvin radii) smaller than that corresponding
326 to the RH of 0.95 but bigger interior radii (bearing in mind the simplified “ink-bottle”
327 pore model and the desorption is controlled by the pore entry or neck sizes [2]) are
328 still filled with water. This explains why higher moisture content at the same RH is
329 observed on the original isotherm compared with that of the scanning curve. As the RH

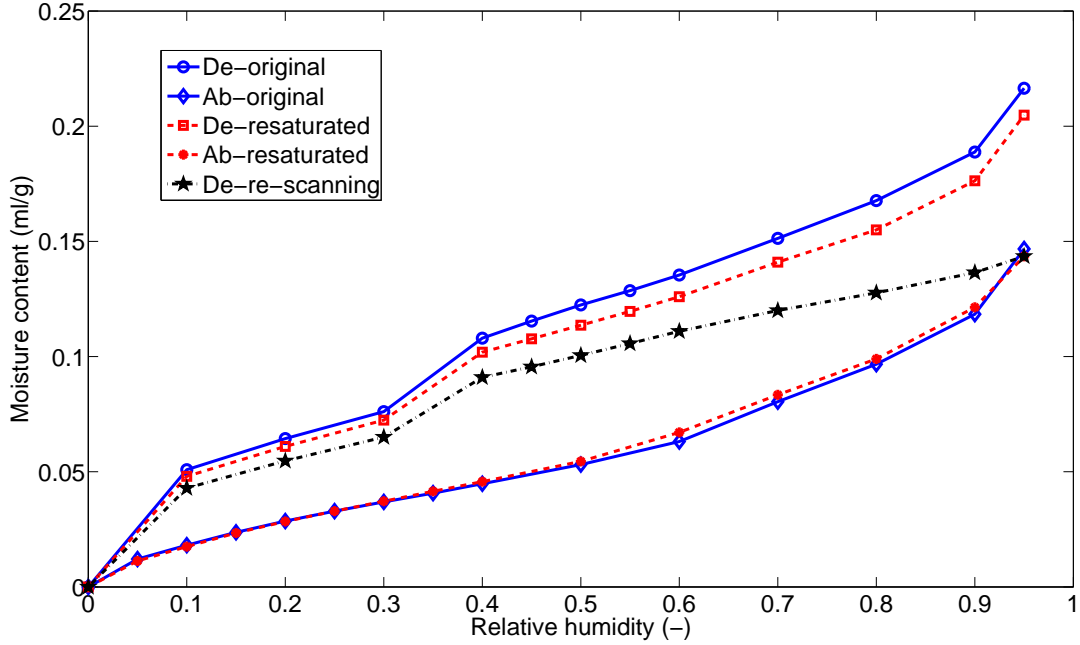


Figure 9: The sorption isotherms (after data extrapolation) for the hardened cement paste sample CEM I. The 'De-original' and 'Ab-original' isotherms are from the first desorption-absorption cycle. The 'De-resaturated' and 'Ab-resaturated' isotherms are the measurements following the sample resaturation. The 'De-re-scanning' is a desorption scanning curve from RH = 0.95 following the 'Ab-resaturated' isotherm.

330 decreases, the volume of the moisture content which stays undesorbed in the relatively
 331 big pores but with small pore entries (or the “ink-bottle” pores for simplicity) also
 332 decreases, resulting into smaller and smaller difference between the original desorption
 333 isotherm and the scanning curve. That is, the difference is probably mainly caused by
 334 the unfilled “ink-bottle” pores. Therefore, if the resaturation can fully saturate all the
 335 big pores, it can be expected that there should be no difference between the original
 336 desorption isotherm and the one of the resaturated sample.

337 By looking at the desorption isotherms, it can be found that there is a somewhat
 338 significant change in terms of the moisture content at the RH of about 0.4. It might
 339 indicate that something possibly occurs around the RH at this level, e.g., the possible

340 conversion of the loose-packed C-S-H particles as discussed by Jennings et al. [12–14]. If
341 this is the case, it can be expected that no permanent changes of the pore structure takes
342 place since the desorption isotherm after resaturation is almost identical to the original
343 isotherm in all essential parts. If the microstructure changes due to the drying at low
344 RHs are relevant in this context, the results in this study tend to support the statement
345 given by Baroghel-Bouny [1] which claims that the reversibility of the microstructure
346 changes, while they are not in accordance with the argument saying that the drying at
347 low RHs changes the microstructure permanently. Additionally, it is also noticed that
348 studies of hardened cement pastes using both small-angle X-ray scattering (SAXS) [27]
349 and small-angle neutron scattering (SANS) [28] indicate that the surface area and the
350 C-S-H gel structure can be fully recovered upon the rewetting of a D-dried specimen.
351 It should be mentioned that the conclusion of permanent microstructure changes of
352 cement paste samples at low RHs is often drawn based on the studies using desiccator
353 method with saturated salt solutions, e.g., see [11, 12, 15]. Using the desiccator method,
354 it often takes long time for the equilibrium to be established at one RH. Thus, it might
355 be reasonable to consider that the permanent microstructure changes as reported in
356 some studies are related to the long time exposure at low RHs, which may enhance
357 the aging effect as discussed by Jennings et al. [12], meaning the so-called irreversible
358 pore structure collapse may not be solely caused by the drying effect at low RHs itself.
359 This argument is supported by the studies using methods with short RH exposure
360 time, such as the DVS, SAXS [27] and SANS [28], which do not show the permanent
361 microstructure changes of cement paste samples at low RHs. To further validate the
362 argument, DVS measurements can be applied to cement paste samples which have been
363 exposed to a certain (low) RH, e.g., 0.30 or 0.40, for relatively a long time (on the order

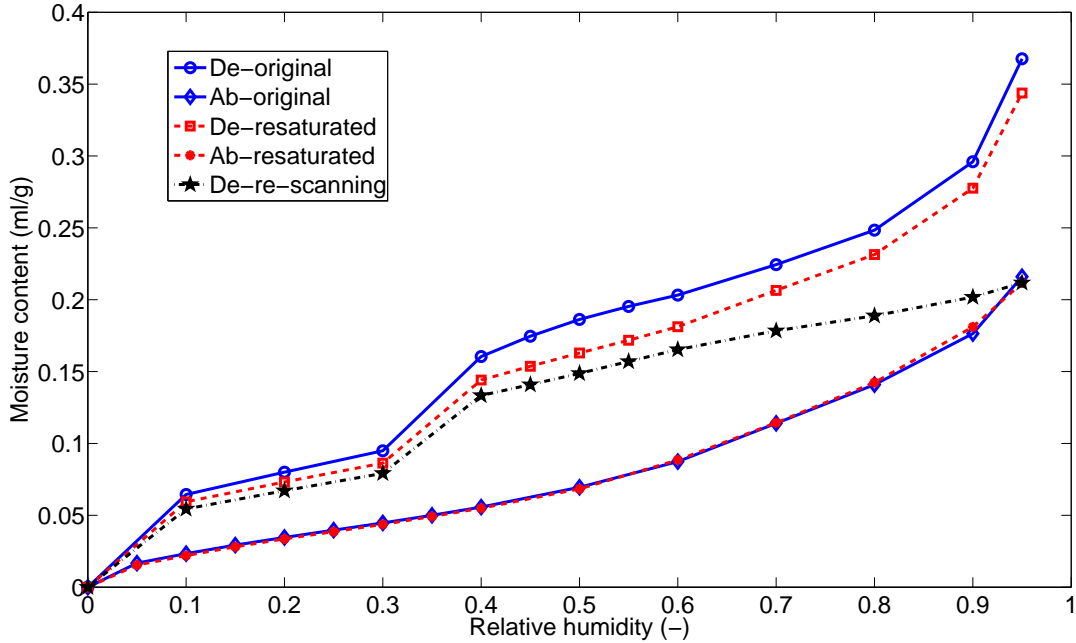


Figure 10: The sorption isotherms (after data extrapolation) for the hardened cement paste sample CEM III. The 'De-original' and 'Ab-original' isotherms are from the first desorption-absorption cycle. The 'De-resaturated' and 'Ab-resaturated' isotherms are the measurements following the sample resaturation. The 'De-re-scanning' is a desorption scanning curve from RH = 0.95 following the 'Ab-resaturated' isotherm.

364 of several months). By comparing the results of the "undried" and "dried" samples, the
 365 effect of drying at low RHs for relatively extended period of time can be obtained.

366 The study indicates that either the drying at low RHs during the desorption mea-
 367 surement does not cause any microstructure changes or if the microstructure changes
 368 do occur, the absorption process must have been able to restore the pore structure
 369 of hardened cement paste samples, meaning the possible microstructure changes are
 370 reversible.

371 3.4. Temperature dependent sorption isotherms

372 Three different temperatures, 25 °C, 33 °C and 40 °C, were considered in this
 373 study. Same as the resaturation study, each measurement was conducted only once.

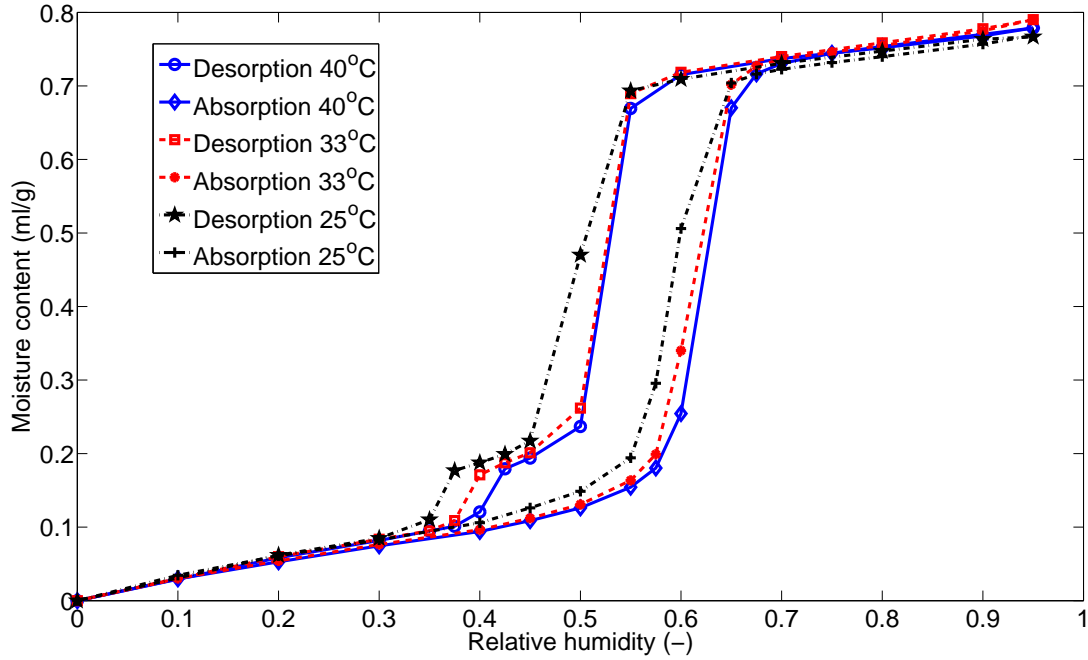


Figure 11: The temperature dependent sorption isotherms for MCM-41 measured at 25 °C, 33 °C and 40 °C. The moisture content is expressed as gram water per gram of dry material and the mass of the dry sample is determined at the point where RH = 0.

374 The absorption and the desorption isotherms (after data extrapolation to equilibrium)
 375 for the MCM-41, CEM I and CEM III are shown in Figure 11, Figure 12 and Figure 13,
 376 respectively. The general trend as reported in the literature is also found for the three
 377 materials studied, i.e., the higher the temperature, the less the amount of absorbed
 378 water. For MCM-41 (Figure 11), the difference between the isotherms at different
 379 temperatures is mainly in the RH range of 0.3-0.7. For hardened cement pastes (Figure
 380 12 and Figure 13), the difference is mainly observed below the RH of about 0.7 in the
 381 desorption isotherms while some small difference can be found above the RH of about
 382 0.5-0.6 in the absorption isotherms. The pronounced differences in the desorption
 383 isotherms obtained for well hydrated concrete as reported in [16–18] were not observed
 384 in this study.

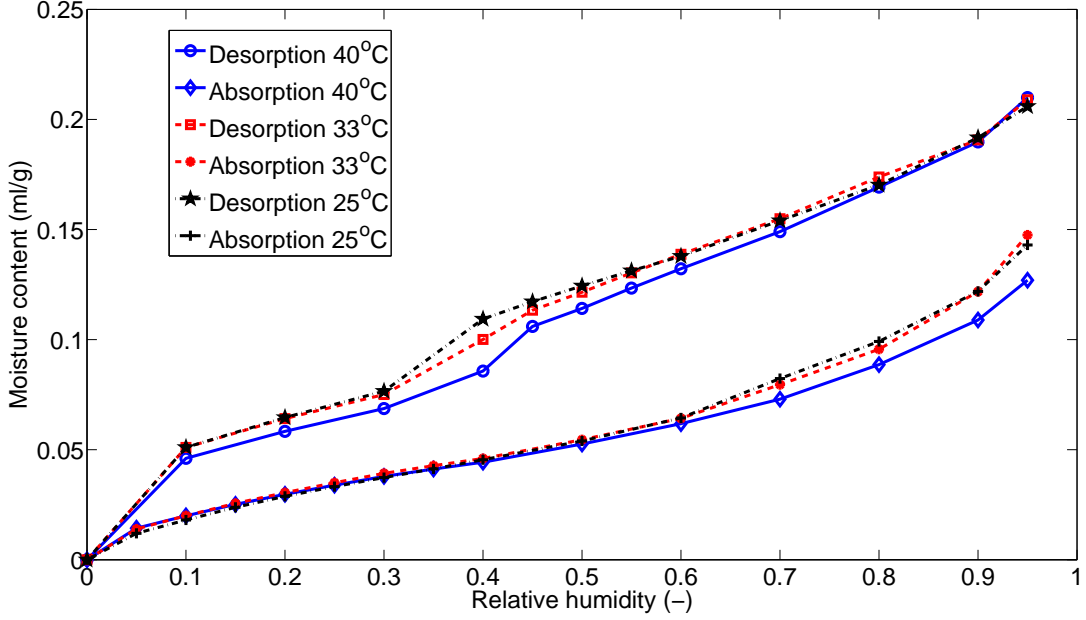


Figure 12: The temperature dependent sorption isotherms for CEM I measured at 25 °C, 33 °C and 40 °C. The moisture content is expressed as gram water per gram of dry material and the mass of the dry sample is determined at the point where RH = 0.

385 To study the influence of the temperature dependent properties of water on the
 386 sorption isotherms, the isotherms at the temperature of 33 °C and 40 °C can be roughly
 387 extrapolated from the measured isotherm (absorption or desorption) under 25 °C by
 388 assuming all water to be capillary condensed water and using the Kelvin equation which
 389 is [8]

$$\frac{1}{r_{k1}} + \frac{1}{r_{k2}} = -\frac{RT\rho_w}{M_w\gamma_w}\ln(\phi) \quad (2)$$

390 where M_w , γ_w and ρ_w is the molecular weight, surface tension of the liquid-gas interface
 391 and the density of water, respectively; ϕ is the RH, R the gas constant and T the
 392 temperature in Kelvin degree; r_{k1} and r_{k2} denote the two principal radii of the curvature
 393 of the liquid meniscus and the contact angle is assumed as zero. The temperature

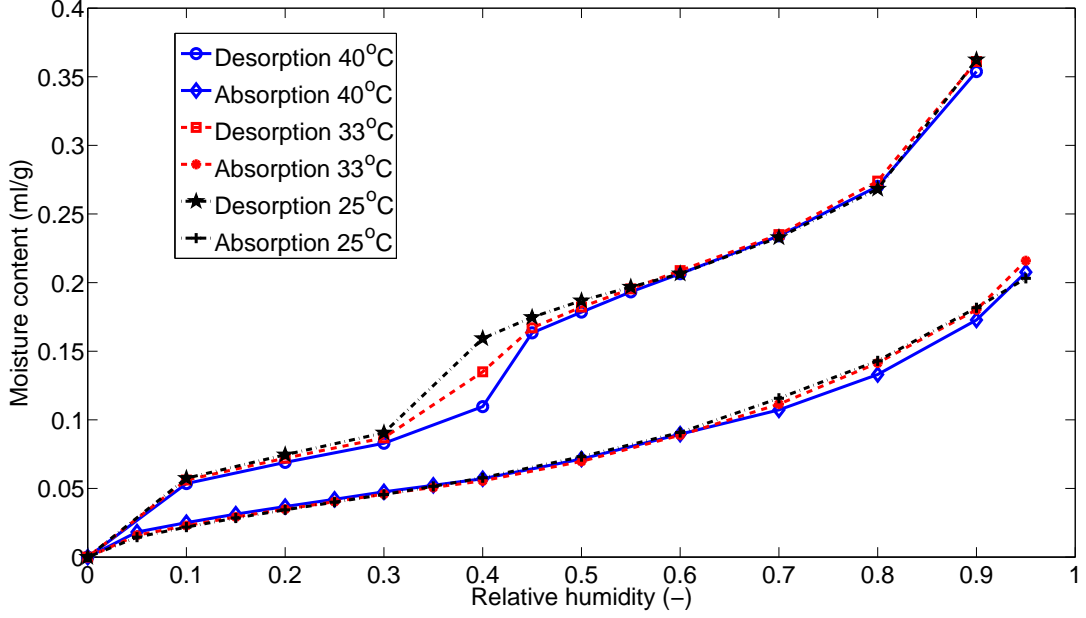


Figure 13: The temperature dependent sorption isotherms for CEM III measured at 25 °C, 33 °C and 40 °C. The moisture content is expressed as gram water per gram of dry material and the mass of the dry sample is determined at the point where RH = 0.

394 dependence of the surface tension and density of water are considered following Eq.3
 395 (in the unit of N/m) [29] and Eq.4 (in the unit of kg/m³) [30], respectively.

$$\gamma_w = (-0.0167t + 7.598) \cdot 10^{-2} \quad (3)$$

396

$$\rho_w = 2 \cdot 10^{-5}t^3 - 0.006t^2 + 0.0227t + 999.94 \quad (4)$$

397 where $t = T - 273.15$ ($0 < t < 100$). For the same radius of a curvature, the corre-
 398 sponding relative humidity will be changed according to the Kelvin equation Eq.2 at
 399 different temperatures. The shift of the relative humidity can be expressed as

$$\ln(\phi_2) = \frac{T_1 \rho_w 1 \gamma_w 2}{T_2 \rho_w 2 \gamma_w 1} \ln(\phi_1) \quad (5)$$

400 where the index 1 and 2 indicate the properties under two different temperatures. By

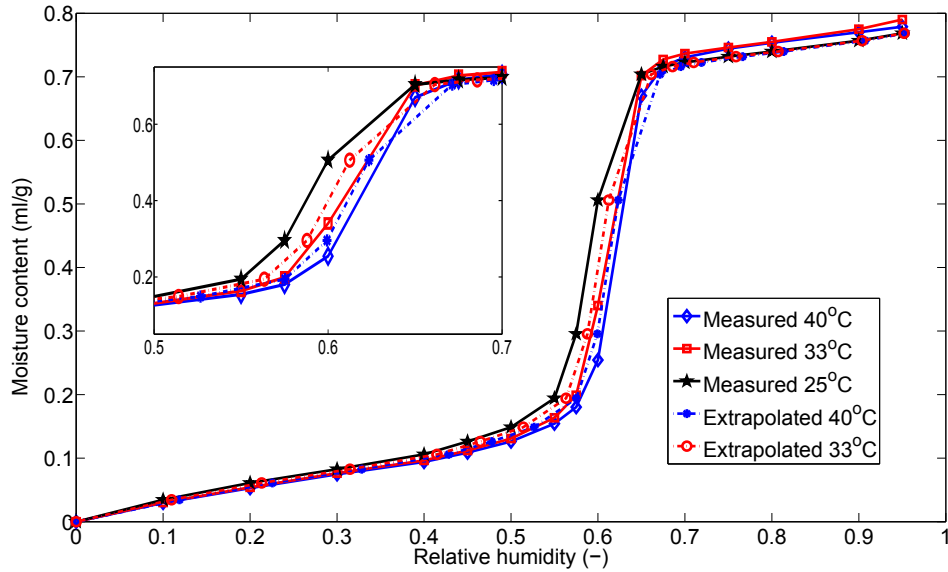


Figure 14: The comparison between the measured and the temperature extrapolated absorption isotherms for MCM-41 under the temperature 33 °C and 40 °C. The extrapolation is based on the isotherm measured at 25 °C according to Eq.5.

401 plotting the moisture content measured under T_1 (corresponding to 25 °C in this case)
 402 against the calculated relative humidity ϕ_2 (corresponding to 33 °C or 40 °C in this
 403 case), the impact of the temperature dependent properties of water on the sorption
 404 isotherms can be estimated. It should be mentioned that this extrapolation does not
 405 distinguish the adsorbed water and capillary condensed water and assumes all the water
 406 is capillary condensed, thus it is just an approximation.

407 The comparison between the measured and the extrapolated isotherms (based on
 408 the isotherm measured at 25 °C) at the temperature 33 °C and 40 °C for MCM-41 are
 409 shown in Figure 14 (absorption) and Figure 15 (desorption). It can be observed that
 410 the temperature dependent properties of water can account for most of the observed
 411 temperature effect on the measured sorption isotherms. For the two hardened cement

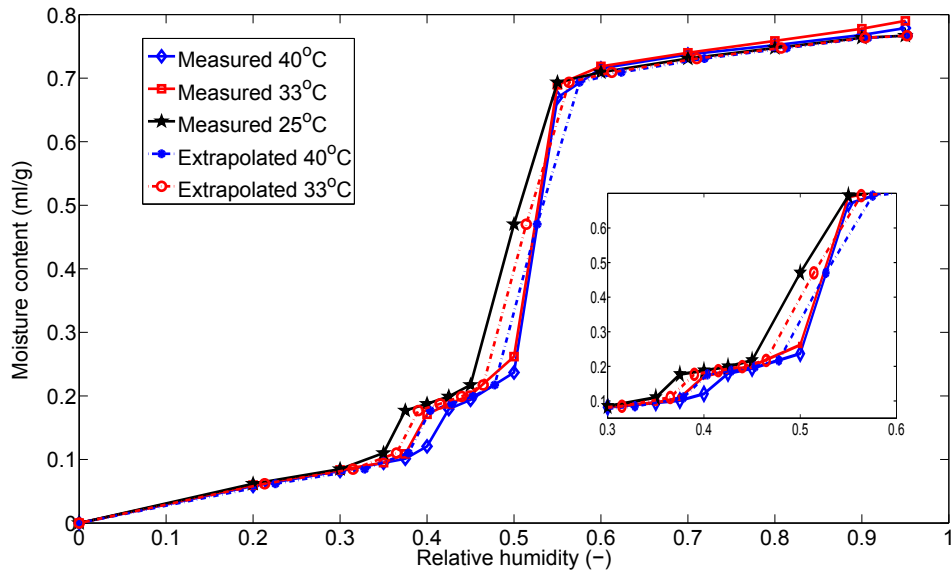


Figure 15: The comparison between the measured and the temperature extrapolated desorption isotherms for MCM-41 under the temperature 33 °C and 40 °C. The extrapolation is based on the isotherm measured at 25 °C according to Eq.5.

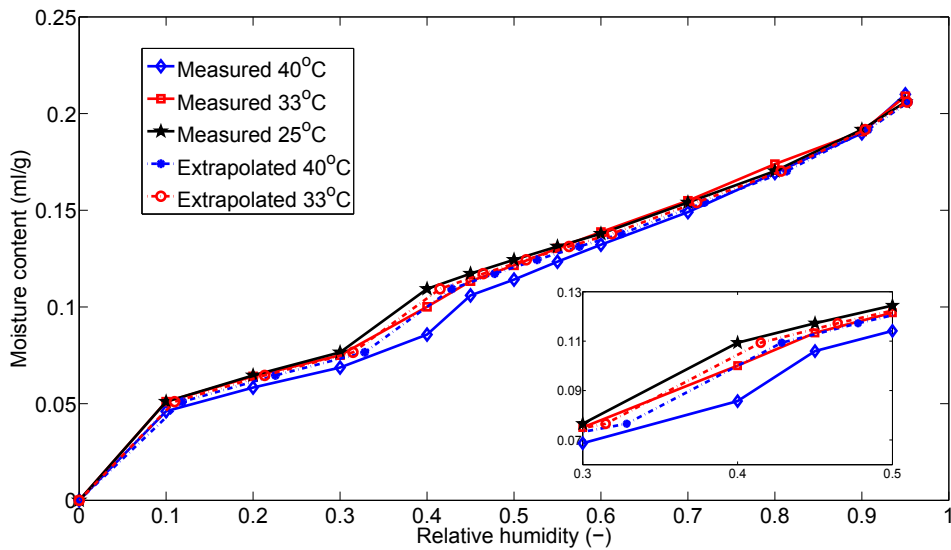


Figure 16: The comparison between the measured and the temperature extrapolated desorption isotherms for CEM I under the temperature 33 °C and 40 °C. The extrapolation is based on the isotherm measured at 25 °C according to Eq.5.

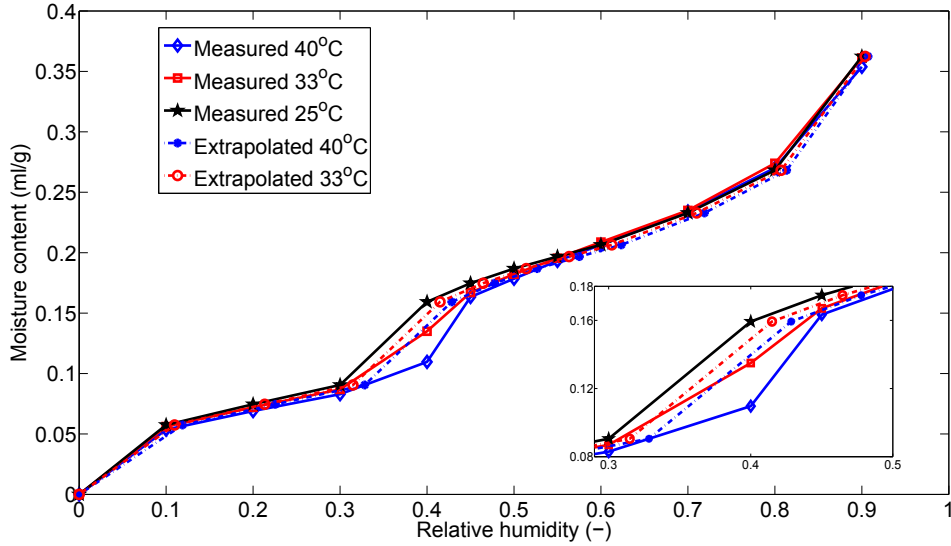


Figure 17: The comparison between the measured and the temperature extrapolated desorption isotherms for CEM III under the temperature 33 °C and 40 °C. The extrapolation is based on the isotherm measured at 25 °C according to Eq.5.

412 pastes, the measured and the extrapolated desorption isotherms are shown in Figure
 413 16 (for CEM I) and Figure 17 (for CEM III), respectively. Again the temperature de-
 414 pendent properties of water can account for some of the observed temperature effect on
 415 the measured sorption isotherms. However, there are still some differences between the
 416 measured and the extrapolated desorption isotherms, especially when the RH is in the
 417 range of 0.3-0.5, indicating that solely taking into account the temperature dependent
 418 properties of water might not be able to explain all the differences. It should be noted
 419 that the remaining differences may be due to the adsorbed layer which is not consid-
 420 ered in the extrapolation as mentioned earlier. Compared with the results for MCM-41
 421 in which limited differences are found between extrapolated and measured isotherms
 422 (silica gel is considered as temperature resistant with respect to the pore volumes and
 423 shape at the adopted measuring temperatures), it tends to motivate that may be the el-

424 evated temperature slightly change the microstructure of the studied hardened cement
425 paste samples, as discussed in [22, 23]. The extrapolations on the absorption isotherms
426 for the two hardened cement pastes are not presented here. However, a close check of
427 Figure 12 and Figure 13 shows that the moisture contents measured at 33 °C and 40
428 °C below the RH of about 0.5 are slightly higher than that measured at 25 °C. This is
429 not in accordance with what is predicted by considering the temperature effect, which
430 is that lower moisture content should be measured at a higher temperature. Hence,
431 the volume of the pores whose corresponding capillary condensation relative pressures
432 are lower than 0.5 might be increased slightly at the elevated measuring temperatures,
433 which is somewhat similar to the effect caused by the drying as reported in [1].

434 The current study regarding the influence of the temperature on the sorption
435 isotherms of hardened cement pastes suggests that the differences in the sorption
436 isotherms at different temperatures are mainly caused by the temperature dependent
437 properties of water and to some extent due to slight microstructure changes of the
438 paste samples at elevated temperatures. The pronounced impact of temperature on
439 desorption isotherms of cement based materials as reported in [16–18] are not found in
440 this study.

441 It should be mentioned that the exact reasons for the relatively inconsistent results
442 with respect to the impact of temperature on sorption isotherms of cement based ma-
443 terials as reported in literature are not clear. However, it might possibly be related to
444 the measurement method adopted. As mentioned before, desiccator method using salt
445 solution has been adopted in many sorption studies, e.g., in [16–21], in which the expo-
446 sure time at each RH varies from several weeks to months for the equilibrium condition
447 to be established. The different length of the exposure time at different RHs combined

448 with the effect caused by different temperatures during measurements (especially when
449 the measuring temperature is high) could possibly change the pore structure of the
450 studied cement based material to a different extent. That is, the pore structure of the
451 studied material may differ under each studied RH, due to the adopted experimental
452 method (procedures). The argument is supported by a recent SANS study [31] which
453 showed that curing at elevated temperature could result into the changing of the pore
454 structure and extended curing at 20 °C had a similar effect. Since the exposure time
455 and the temperature differ in studies, e.g., in [16–21], it is somewhat not surprising to
456 see the inconsistent results as reported. One advantage of the DVS method used in this
457 study is that the exposure time at each RH is relatively short. Then, the effect due to
458 the pore structure changes during sorption measurements is expected to be minimized.

459 **4. Conclusions**

460 Water vapor sorption isotherms measured by the “dynamic vapor sorption” (DVS)
461 method were used to investigate the possible changes of the pore structure of hardened
462 cement pastes (CEM I and CEM III) subjected to low relative humidities. In addition,
463 the temperature dependency of the sorption isotherms was investigated. Some key
464 points of this investigation can be summarized as follows.

- 465 1. Small differences were observed between the sorption measurements on a model
466 material MCM-41 using different samples. Similarly, only small differences were
467 observed for the investigated hardened cement pastes which indicates that the
468 hardened cement paste samples only to a very limited extent hydrated further
469 during the period of the investigation (about 3-4 months).
- 470 2. A resaturation study on the hardened cement paste samples was conducted in

471 order to investigate the possible microstructure changes caused by the drying at
472 low RHs during desorption measurements. Following the first original desorption-
473 absorption cycle, the samples were resaturated and a second desorption measure-
474 ment was performed. The measurement results show that the second desorption
475 isotherm was in all essential parts similar to the first one. That is, either the dry-
476 ing did not cause any microstructure changes during the desorption at low RHs
477 or if the microstructure changes did occur, the absorption process must have been
478 able to restore the pore structure of hardened cement paste samples. The latter
479 is in agreement with the results obtained using small-angle X-ray scattering mea-
480 surements [27], small-angle neutron scattering measurements [28] and the findings
481 in [1]. But it also disagrees with some other studies, e.g., [11–13, 15]

482 3. The influence of temperature on the sorption isotherms was studied. Only lim-
483 ited impact was observed and the results suggest that the differences between
484 sorption isotherms under different temperatures are mainly caused by the tem-
485 perature dependent properties of water. The pronounced impact of temperature
486 on desorption isotherms of cement based materials as reported in [16–18] was not
487 found.

488 **Acknowledgment**

489 The research leading to these results has received funding from the European Union
490 Seventh Framework Programme (FP7/2007-2013) under grant agreement 264448.

491 [1] V. Baroghel-Bouny. Water vapour sorption experiments on hardened cementitious
492 materials: Part I: Essential tool for analysis of hygral behaviour and its relation
493 to pore structure. *Cement and Concrete Research*, 37(3):414–437, 2007.

- 494 [2] N.A. Seaton. Determination of the connectivity of porous solids from nitrogen
495 sorption measurements. *Chemical Engineering Science*, 46(8):1895–1909, 1991.
- 496 [3] V. Baroghel-Bouny. Water vapour sorption experiments on hardened cementitious
497 materials. Part II: Essential tool for assessment of transport properties and for
498 durability prediction. *Cement and Concrete Research*, 37(3):438–454, 2007.
- 499 [4] V. Baroghel-Bouny, M. Mainguy, and O. Coussy. Isothermal drying process in
500 weakly permeable cementitious materials- assessment of water permeability. In
501 *International Conference on Ion and Mass Transport in Cement-Based Materials*,
502 pages 59–80, 1999.
- 503 [5] V. Baroghel-Bouny, M. Mainguy, T. Lassabatere, and O. Coussy. Characterization
504 and identification of equilibrium and transfer moisture properties for ordinary and
505 high-performance cementitious materials. *Cement and Concrete Research*, 29(8):
506 1225–1238, 1999.
- 507 [6] M. Thiery, V. Baroghel-Bouny, G. Villain, and P. Dangla. Numerical modeling
508 of concrete carbonation based on durability indicators. In V.M. Malhotra, editor,
509 *Proceedings of the 7th CANMET/ACI International Conference on Durability of*
510 *Concrete*, pages 765–780, 2006.
- 511 [7] B. Bary and A. Sellier. Coupled moisture–carbon dioxide–calcium transfer model
512 for carbonation of concrete. *Cement and Concrete Research*, 34(10):1859–1872,
513 2004.
- 514 [8] K. Sing, D. Everett, R. Haul, L. Moscou, R. Pierotti, J. Rouquerol, and T. Siemie-

- 515 niewska. Reporting physisorption data for gas/solid systems. *Pure Appl. Chem*,
516 57(4):603–619, 1985.
- 517 [9] M. Janz and B.F. Johannesson. Measurement of the moisture storage capacity
518 using sorption balance and pressure extractors. *Journal of Building Physics*, 24
519 (4):316–334, 2001.
- 520 [10] V. Kocherbitov and L. Wadsö. A desorption calorimetric method for use at high
521 water activities. *Thermochimica Acta*, 411(1):31–36, 2004.
- 522 [11] R.F. Feldman. Sorption and length-change scanning isotherms of methanol and
523 water on hydrated portland cement. In *Proc. of 5th Int. Congress on the Chemistry*
524 *of Cement*, volume 3, pages 53–66. Cem. Assoc. of Japan, Tokyo, 1968.
- 525 [12] H.M. Jennings. A model for the microstructure of calcium silicate hydrate in
526 cement paste. *Cement and Concrete Research*, 30(1):101–116, 2000.
- 527 [13] J.J. Thomas and H.M. Jennings. A colloidal interpretation of chemical aging of the
528 C-S-H gel and its effects on the properties of cement paste. *Cement and Concrete*
529 *Research*, 36(1):30–38, 2006.
- 530 [14] H.M. Jennings. Refinements to colloid model of C–S–H in cement: CM–II. *Cement*
531 *and Concrete Research*, 38(3):275–289, 2008.
- 532 [15] E.H. Atlassi. Influence of silica fume on the pore structure of mortar when mea-
533 sured by water vapour sorption isotherms. In *The Modelling of Microstructure*
534 *and its Potential for Studying Transport Properties and Durability*, pages 257–270.
535 Springer, 1996.

- 536 [16] S. Poyet. Experimental investigation of the effect of temperature on the first
537 desorption isotherm of concrete. *Cement and Concrete Research*, 39(11):1052–
538 1059, 2009.
- 539 [17] S. Poyet and S. Charles. Temperature dependence of the sorption isotherms of
540 cement-based materials: Heat of sorption and Clausius–Clapeyron formula. *Ce-
541 ment and Concrete Research*, 39(11):1060–1067, 2009.
- 542 [18] J. Hundt and H. Kantelberg. Sorptionsuntersuchungen an zementstein, zementmör-
543 tel und beton (in German). *Deutscher Ausschuss für Stahlbeton*, 297:25–39, 1978.
- 544 [19] J.F. Daian. Condensation and isothermal water transfer in cement mortar, Part
545 I–pore size distribution, equilibrium water condensation and imbibition. *Transport
546 in Porous Media*, 3(6):563–589, 1988.
- 547 [20] F. Radjy, E.J. Sellevold, and K.K. Hansen. Isoteric vapor pressure–temperature
548 data for water sorption in hardened cement paste: enthalpy, entropy and sorption
549 isotherms at different temperatures. Technical Report BYG-DTU R057, Technical
550 University of Denmark(DTU), Lyngby, Denmark, 2003.
- 551 [21] T. Ishida, K. Maekawa, and T. Kishi. Enhanced modeling of moisture equilibrium
552 and transport in cementitious materials under arbitrary temperature and relative
553 humidity history. *Cement and Concrete Research*, 37(4):565–578, 2007.
- 554 [22] Z.P. Bazant and W. Thonguthai. Pore pressure and drying of concrete at high
555 temperature. *Journal of the Engineering Mechanics Division*, 104(5):1059–1079,
556 1978.

- 557 [23] B. Bary. A polydispersed particle system representation of the porosity for non-
558 saturated cementitious materials. *Cement and Concrete Research*, 36(11):2061–
559 2073, 2006.
- 560 [24] B. Johannesson. Moisture fixation in mature concrete and other porous materials
561 (8A). Lecture notes for Introduction to Concrete Technology (11563), Technical
562 University of Denmark, 2011.
- 563 [25] H.H. Willems and K.B. Van Der Velden. A gravimetric study of water vapour
564 sorption on hydrated cement pastes. *Thermochimica Acta*, 82(1):211–220, 1984.
- 565 [26] M. Åhs. *Redistribution of moisture and ions in cement based materials*. PhD
566 thesis, Division of Building Materials, Lund University, 2011.
- 567 [27] D.N. Winslow and S. Diamond. Specific surface of hardened portland cement paste
568 as determined by small-angle X-ray scattering. *Journal of the American Ceramic*
569 *Society*, 57(5):193–197, 1974.
- 570 [28] D. Pearson and A.J. Allen. A study of ultrafine porosity in hydrated cements using
571 small angle neutron scattering. *Journal of Materials Science*, 20(1):303–315, 1985.
- 572 [29] Engineeringtoolbox, . URL [http://www.engineeringtoolbox.com/
573 water-surface-tension-d_597.html](http://www.engineeringtoolbox.com/water-surface-tension-d_597.html). Accessed on December 13, 2012.
- 574 [30] Engineeringtoolbox, . URL [http://www.engineeringtoolbox.com/
575 water-density-specific-weight-d_595.html](http://www.engineeringtoolbox.com/water-density-specific-weight-d_595.html). Accessed on December 13,
576 2012.

- 577 [31] H.M. Jennings, J.J. Thomas, J.S. Gevrenov, G. Constantinides, and F.-J. Ulm.
578 A multi-technique investigation of the nanoporosity of cement paste. *Cement and*
579 *Concrete Research*, 37(3):329–336, 2007.