Temperature-Dependent Water Redistribution from Large Pores to Fine Pores after Water Uptake in Hardened Cement Paste

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Abstract
During sorption, the microstructural evolutions of two different cement pastes (with water-to-cement ratios of 0.40 and 0.55) are studied via proton-nuclear-magnetic-resonance relaxometry. The water uptake test is performed for samples dried at 105°C under three different temperatures of 20°C, 40°C, and 60°C for the first twenty-six days of sorption. It is observed that the water went first to the larger pores before migrating to the finest ones. This behavior is accelerated with increasing temperature. The rate of water exchange between fine and large pores is estimated and found to increase with temperature for both studied mixtures. The activation energy corresponding to this water movement is calculated and found to be higher for the lowest water-to-cement ratio, owing its finer microstructure. Finally, the activation energy related to the local water transport in re-distribution from large pores to fine pores is calculated and found to be inferior to the experimental results, which can be explained by the dynamic microstructure not being considered in the classical theories.

1. Introduction
After the Fukushima Daiichi nuclear disaster in 2011, a project was undertaken to understand the fundamental mechanisms behind ion transport and the interaction between ions and concrete components, with the goal of aiding the decontamination, shielding, and disposal of concrete members affected by cesium and strontium at the nuclear power plant. For this, a reliable evaluation of the depth of cesium and strontium penetration in reactor building concrete was required. To achieve this objective, a critical phenomenon to consider is the water transport and microstructure change in such unsaturated media.

The concrete in the nuclear infrastructure at Fukushima was dried over many years of service before the 2011 incident. Then, portions of the concrete surfaces were completely immersed in liquid water, going from a dried state to a saturated state via the water absorption process. For a typical case with no interaction between the fluid and the material, the fluid transport should only depend on the liquid viscosity and the surface tension reflecting the intrinsic pore structure. This dependency is also observable for cement-based materials in capillary absorption tests when organic fluids are used, such as n-heptane, n-decane, n-dodecane, and ethanol however, when the fluid is water, the two-parameter dependency is no longer valid (Hall et al. 1995; Taylor et al. 1999). A drop in the measured rate of water absorption compared to the theoretical prediction has been observed with a sorptivity that is lower by a factor between 1.5 and 2.

This special behavior of water transport in cement-based materials is generally qualified as “anomalous” (Martys and Ferraris 1997; Hall 2007), and should be distinguished from the saturation-dependent diffusivity, the sorption hysteresis, and the irreversibility of the first sorption cycle. This behavior was previously explained by a blockage in the porous network, which can have different origins. The clearest is the delayed hydration of unreacted and dehydrated elements that creates new calcium silica hydrate (C-S-H) layers. For the origin of this behavior, the precipitation of the calcium hydroxide has also been suggested, as well as the swelling of the hydrate gel in contact with water. Additionally, microcracking caused by drying and shrinkage during the pretreatment phase are indicated to be susceptible areas to these microstructural modifications.

Recently, based on the proton nuclear magnetic resonance (¹H-NMR) relaxometry technique, the dynamic
change in microstructure accompanying water adsorption has been considered as the main mechanism of the anomalous behavior of water uptake (McDonald et al. 2020). Indeed, by using water and n-decane as liquids for a sorption test, a rearrangement of the porosity has only been observed in the case of water, suggesting the existence of an indirect link between the dynamic porosity and anomalous water transport. This result was also supported by the successful modeling of the anomalous water absorption when the dynamic porosity considering saturation and history was integrated (McDonald et al. 2020). Water movement in cement-based materials is dominated by the smallest pores with the smallest diffusivity and any variation in its microstructure will have important impacts on the apparent global transport coefficient. Under saturation conditions, the distribution of the pore sizes changes with the collapse of pores with time and many attempts to quantify this have been presented in previous studies (Gajewicz et al. 2016; Zhou et al. 2017, 2018; Holthausen and Raupach 2018; Maruyama and Rymeš 2019).

The water redistribution ability of C-S-H between interlayer spaces and gel pores is now well known (McDonald et al. 2005; Valori et al. 2010, 2013), and is related to the colloidal nature of C-S-H (Jennings 2000, 2008; Maruyama et al. 2015). Moreover, recent studies have presented advanced characterizations allowing a better understanding of the impact of different parameters on the water exchange process. For instance, the effect of pre-drying at 40°C and 105°C shows stronger consolidation of gel pores at 105°C, preventing a fast swelling (Schulte Holthausen and Raupach 2018). Another example is the influence of drying conditions (relative humidity) on the dynamic microstructural evolution for the first drying (Muller et al. 2013a; Maruyama et al. 2019). The effect of mixture parameters can also be observed, such as the influence of supplementary cementitious materials on the microstructure modification (silica fume in the works of McDonald et al. (2005) and Muller et al. (2015).

In the context of nuclear power plants, capturing the temperature dependency of this dynamic microstructure (related data has been reported by Maruyama and Rymeš (2019)) is critical for a more accurate estimation of the moisture transport, such as in a recent trial by Li and Xu (2019). To the authors’ knowledge, no similar data for the water redistribution ability of C-S-H between large and fine pores is calculated for three different temperatures. For many parameters with temperature dependency (such as permeability, diffusion, creep, and cracking), Arrhenius behavior can be observed. Thus, the activation energy of the rate of the internal water transport is estimated, allowing a better interpretation of the measurements.

2. Experimental methods

2.1 Materials

White Portland cement provided by Taiheiyo Cement Corporation was used to prepare the hcp. As 1H-NMR relaxometry is affected by paramagnetic ions such as iron and magnesium, white Portland cement containing only trace amounts of iron or magnesium was used in this study. The chemical composition was determined by the X-ray fluorescence (XRF) method and the mineral composition of the white Portland cement were performed by X-ray powder diffraction (XRD) on a powder sample. D8 advance equipment was used for the X-ray powder diffraction (XRD) and the TOPAS software was used for the Rietveld analysis, as shown in Tables 1 and 2, respectively. It should be noted that there is a small proportion or a non-detectable quantity of magnetic oxides (Fe2O3 and Mn2O3) contributing to the transverse NMR relaxation (Miljkovic et al. 1988). All the materials were stored in a thermostatic room and the temperature was controlled at 20 ± 1°C for one day prior to mixing. The mixing was performed at room temperature. The water-to-cement ratios of the specimens were set as 0.40 and 0.55 (hereinafter denoted as W40 and W55). These values cover the water to binder ratios of concrete used in Fukushima daiichi nuclear power plants (Kaburagi 1969). The paste was mixed using a planetary centrifugal mixer at 1000 rpm for 1.5 min after the water was added to the cement. Next, the paste was scraped to detach residual powder from the
internal surface of the mixer, and finally an additional 1.5 min of mixing was performed. After the mixing, the paste was immediately moved to the thermostatic room at 20 ± 1°C and remixed every 30 min for 8 h to minimize segregation. All samples were sealed and cured after being poured into the cylindrical plastic container (ϕ 30 mm × 125 mm). After ninety-one days, the plastic container was demolded, and specimens cored to a size of ϕ 4.5 mm × 5 mm and kept at room temperature.

2.2 Method for water absorption
The 1H-NMR relaxometry was performed for the obtained samples in the sealed condition, after vacuum drying, and in the water absorption process. During each measurement, the mass of the sample was measured using a precision balance. Vacuum drying with a degasser (FLOVAC, Quantachrome) was used for the drying treatment. In the vacuum drying, the specimen was kept at 105°C for one day and then 1H-NMR relaxometry was performed. During the water absorption process, the water to solid ratio was more than 20, the calcium hydroxide saturation water was used, and its temperature was maintained at 20°C, 40°C, and 60°C. The temperature inside the device was controlled so that the temperature at the time of the 1H-NMR relaxometry measurement was equal to the temperature of the absorbed water. Curing water was used for the water absorption process and vacuum absorption was performed for 30 min after the drying treatment. For the subsequent water absorption, curing water was stored at each temperature and, after that, the samples were stored as shown in Fig. 1 and removed from the submerged water immediately before the 1H-NMR measurement. Immediately before the measurement, the water on the sample was wiped off and the Carr–Purcell–Meiboom–Gill (CPMG) measurement was performed. The CPMG echo signal was measured after 30 min, 1 day, 2 days, 5 days, 12 days, and 26 days at different temperatures. Three samples were used for each temperature.

2.3 1H-NMR relaxometry method
The 1H-NMR relaxometry was carried out at Nagoya University in Japan and was conducted using a Bruker minispec equipped with a digital filter and a ϕ 10 mm probe. After coring, the cement paste specimen size of ϕ 4.5 mm × 5 mm was kept in a glass rod has a diameter 4.5 mm × 5 mm and kept at room temperature. The 1H-NMR relaxometry was performed for the obtained samples in the sealed condition, after vacuum drying, and in the water absorption process. During each measurement, the mass of the sample was measured using a precision balance. Vacuum drying with a degasser (FLOVAC, Quantachrome) was used for the drying treatment. In the vacuum drying, the specimen was kept at 105°C for one day and then 1H-NMR relaxometry was performed. During the water absorption process, the water to solid ratio was more than 20, the calcium hydroxide saturation water was used, and its temperature was maintained at 20°C, 40°C, and 60°C. The temperature inside the device was controlled so that the temperature at the time of the 1H-NMR relaxometry measurement was equal to the temperature of the absorbed water. Curing water was used for the water absorption process and vacuum absorption was performed for 30 min after the drying treatment. For the subsequent water absorption, curing water was stored at each temperature and, after that, the samples were stored as shown in Fig. 1 and removed from the submerged water immediately before the 1H-NMR measurement. Immediately before the measurement, the water on the sample was wiped off and the Carr–Purcell–Meiboom–Gill (CPMG) measurement was performed. The CPMG echo signal was measured after 30 min, 1 day, 2 days, 5 days, 12 days, and 26 days at different temperatures. Three samples were used for each temperature.

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The CPMG pulse sequence method proposed by (Carr and Purcell 1954) and modified by (Meiboom and Gill 1958) was used for all the measurements to obtain the distribution of T2 relaxation time based on the CPMG echo sequence decay. The device was connected to the water bath where the temperature was maintained throughout the experiment. Blank cell correction at each temperature was performed. Two-hundred log-spaced echoes were recorded from 0.1 to 2180 ms and more than 256 averages were recorded to obtain a sufficient signal-to-noise ratio. To record the CPMG pulse sequence and solid echo signal took approximately 1 h and 45 min. The decay curve was obtained by measuring the time required to return to the thermal equilibrium state when the external magnetic field was removed from the excited state (transverse relaxation time: T2). This relaxation time becomes shorter as the constraint becomes stronger. In other words, for water present in the voids, the longer the relaxation time, the larger the void diameter. The measured CPMG data were analyzed with an in-house inverse Laplace transform (ILT) algorithm, using the Butler–Reeds–Dawson (BRD) method (Butler et al. 1981), to obtain the quasi-continuous T2 distributions. As shown in Fig. 2, the four confirmed T2 peaks from the ILT algorithm were used to analyze the CPMG data. The four peaks and the ratio of each peak to the total intensity were used to evaluate the quantities of interlayer water, gel pore water, interhydrate pore water, and capillary pore water (Gajewicz et al. 1999; Muller et al. 2013c). A lower T2 indicates smaller pores.

NMR signals are expected to change with temperature, owing to the temperature dependence of the Boltzmann
factor that contributes to the equilibrium nuclear magnetization. Based on the theory (Chary and Govil 2008; Wyrzykowski et al. 2017), the 60°C/20°C and 40°C/20°C signal ratios were 0.880 and 0.936, respectively, while the obtained CPMG data was normalized by the data at the 20°C condition. It is also assumed that the $T_2$ values at different temperatures are not affected by the temperature of the sample (Wyrzykowski et al. 2017).

The in-situ ¹H-NMR relaxometry is only the technique that can detect the C-S-H dynamic structural change during the water suction among the existing researches. This in-situ technique is different from the other experimental techniques to analyze the pore structure of hcp with pre-treatment of drying, which causes the inevitable microstructure changes due to colloidal nature of C-S-H, such as mercury intrusion porosimetry and nitrogen sorption isotherms. It may be also possible to detect it by using SAXS or SANS, but these techniques require the (synchrotron) radiation facility such as SPring-8 in Japan and hypothesis to extract the information from the obtained profiles.

3. Theory

3.1 Rate of water exchange between large and fine pores

The water in the cement paste can be separated into two categories, the water in either fine or large pores, according to the equation:

$$W_L + W_F = W$$  

where $W_L$ is the water in large pores (capillary pores + interhydrate pores) (g/g-ignited cem), $W_F$ is the water in fine pores (gel pores and interlayer spaces) (g/g-ignited cem), and $W$ is the evaporable water (g/g-ignited cem).

The water redistribution from the large pores to the fine pores during the sorption test can be expressed as:

$$\frac{\partial W_F}{\partial t} = \alpha W_L$$  

where $t$ is the time (days) and $\alpha$ is a coefficient indicating the rate of water redistribution from large pores to fine pores per unit time (1/day).

3.2 Activation energy of the rate of exchange between large and fine pores

In 1889, Arrhenius introduced the concept of activation energy as the minimum energy necessary for a specific chemical reaction to occur. Since then, it has been adapted to many phenomena that are time and temperature dependent. Thus, many phenomena related to the field of cementitious materials were found to be well described by the activation/rate theory. For instance, hydration (Bazant et al. 2004), permeability (Powers 1979), moisture diffusion (Hughes et al. 1966; Hancock 1968), diffusion of ions (Nakashima 1995; Otsuki et al. 2009; Zehtab and Tarighat 2018), creep (Klug and Wittmann 1969; Day and Gamble 1983; Bazant 1988), and even aging of cracked concrete (Pertué et al. 2013) have already been analyzed through this approach. In this study, the activation energy related to the rate of exchange between large and fine pores during the water uptake process will be calculated. An Arrhenius plot in which the logarithm of the rate is plotted against the reciprocal of the absolute temperature will provide this activation energy ($E_a$) divided by the ideal gas constant ($R = 8.314 \text{J.K}^{-1}\text{mol}^{-1}$) as the slope of the curve.

4. Results and discussion

4.1 ¹H-NMR results

The obtained $T_2$ relaxation times for both compositions are presented in Fig. 3. The peaks corresponding to the capillary pore water are difficult to observe in some cases. For a very thin section, the exposure to the atmospheric conditions just before the beginning of the test (on the order of several minutes) can be enough to dry out the capillary pores instantly. Therefore, the capillary pores detected by this approach are expected to be very low (McDonald et al. 2020). The fast diffusion relaxation model links the relaxation time $T_2$ to the pore
surface area $S$ and pore volume $V$ as:

$$\frac{1}{T_2} \geq S \frac{1}{V} \frac{1}{T_{2,\text{surf}}} \sim (3)$$

where $\varepsilon_0$ is the diameter of a water molecule, taken as equal to 0.28 nm, and $T_{2,\text{surf}}$ corresponds to the fast-relaxing molecules on the pore surface. Following the method proposed by Gajewicz (2014), this surface relaxation time is 106 μs. By considering planar pores with area $A$, the pore surface can be expressed as $S = 2A$ and the pore volume can be expressed as $V = Ad$, where $d$ represents the pore width (Muller et al. 2013c). Thus, Eq.(3) becomes:

$$\frac{1}{T_2} \frac{2\varepsilon_0}{d} \frac{1}{T_{2,\text{surf}}} \sim (4)$$

The pore width is clearly proportional to the relaxation time $T_2$ and can provide initial details on the C-S-H microstructure. In the sealed condition, the size of the interlayer space is approximately 1.73 ± 0.08 nm for W40 and approximately 2.07 ± 0.11 nm for W55. Under 105°C drying, most of the water is removed and the remaining fraction in the interlayer space shows a stacked C-S-H structure with an interlayer width equal to 1.24 ± 0.20 nm and 1.20 ± 0.20 nm for W40 and W55, respectively. After wetting, the interlayer spaces of W40 and W55 broaden again, returning after 26 days to their initial sizes of 1.72 ± 0.11 nm and 2.02 ± 0.11 nm, respectively, at 20°C, and to a greater sizes of 1.87 ± 0.05 nm and 2.30 ± 0.00 nm, respectively, at 60°C. The absorption under high temperatures clearly widens the interlayer pores. The same observations can be made for the gel pores with average initial widths of 4.42 ± 0.72 nm and 5.16 ± 0.30 nm for respectively W40 and W55 in the sealed condition. The gel pores become larger after

Fig. 3 $T_2$ distributions calculated by an inverse Laplace transformation of the CPMG signal of W40 and W55 under temperatures of 20°C, 40°C, and 60°C.
wetting, especially for higher temperatures. After 26 days of water absorption for W40 and W55, the calculated widths are equal to 5.21 ± 0.47 nm and 5.71 ± 0.17 nm, respectively, at 20°C; to 5.54 ± 0.19 nm and 6.71 ± 0.10 nm, respectively, at 40°C; and to 5.49 ± 0.39 nm and 7.31 ± 0.07 nm, respectively, at 60°C. For interhydrate and capillary pores, more fluctuation is observed with temperature, which can be explained by the high signal-to-noise ratio and the lower number of detected pores as compared to the finest ones (statistically, a lower representative population).

The evaporable water for different samples was measured with a balance in different conditions. The mass evolutions are presented in Fig. 4. The mass given by the balance and that obtained by the NMR being generally in the same range confirms that all the water is captured by the 1H-NMR. A high evaporable water content was observable for W55 as compared to W40, which is consistent with the initial high water content and consequently the high porosity. For the sealed condition,
the water content was slightly higher as compared to the wetted samples for the different periods of sorption. After drying at 105°C, the evaporable water was almost removed and only a very small quantity remained in the interlayer pores according to the 1H-NMR results. The sample was assumed to be completely dried and its mass used as a reference to estimate the absorbed water from the balance measurements. The influence of temperature on the sorption is not detectable here since a high percentage of the water was already absorbed after the first 30 min.

The water distribution according to the size of pores given by 1H-NMR is also presented in Fig. 4. In the sealed condition, a large amount of the evaporable water is present in the interlayer pores. After drying and rewetting, this initial amount of interlayer water was never again recovered for the various cases. For the temperatures of 20°C and 40°C, the water starts to move to the cement paste via the interhydrate pores before migrating towards the finest pores (interlayer and gel). Under these environmental conditions, the interlayer pores seem to increase slightly with time, which is not the case under 60°C. The starting composition of pore water is consistent to the data by Muller et al. (2013b), and the pore water behavior after water suction confirmed in the present study, that is water is first absorbed in large pores and then distributed to the fine pores, are also the representation of the research by Gajewicz-Jaromin et al. (2019). Consequently, the present data are considered reliable. Regarding the temperature at 60°C, the interhydrate water seems already lower as compared to the gel water after 30 min of water uptake. One explanation for this difference is the increase of the rate of water exchange with temperature, which prevents the initial water state of the sample being attained. At the end of the test (26 days), the interhydrate water becomes negligible and almost all the evaporable water is in the interlayer and gel pores. At this moment, the predominant pores are gel pores except for W40 under 20°C and 40°C for which the water is equally distributed between interlayer and gel pores. The influence of the mixture also appears to be important for the microstructure rearrangement. Indeed, W55 with the highest initial water content and then the highest porosity is better able to contain water in the gel pores not only under the sealed condition but also after rewetting. This result suggests that the porosity of W55 is larger than that of W40 and this order is not affected by the microstructural dynamics. This result can also be obtained via the bulk density of C-S-H, which incorporates the gel pore water. Thus, the bulk density of C-S-H decreases with wetting time. It is also a decreasing function of the water-to-cement ratio, which is consistent with previous data (Muller et al. 2013c). The bulk density appears to decrease with temperature, as the water incorporated in gel pores increases with temperature as compared to interlayer water for both mixtures, but this variation is more pronounced for W55 than W40.

Muller et al. (2013b), studied the sealed curing hardened cement samples after 10 days of hydration with different water to cement ratio (W/C = 0.32, 0.40 and 0.48) and they do not show the capillary pore water. Only at very early age, the capillary pore water can be seen. Based on these backgrounds, sample measurement results of the starting and after 26-day of water suction were consistent to the previous data.

The reasoning can be simplified by classifying the pores into two different categories: fine and large (free water) pores. The fine pores are defined as the summation of the interlayer and gel pores while the large pores are the summation of the interhydrate and capillary pores. The evolution of the water inside the cement paste can now be plotted according to this classification, as shown in Fig. 5. In the sealed condition, the predominant pores were the fine pores and negligible quantities of water were found in the large pores for both mixtures. After drying at 105°C, the large pores were completely emptied while a small quantity of water remained in the fine pores. At the beginning of the wetting phase, the large pores had a maximum evaporable water content, with the quantity decreasing with time until reaching the smallest value at 26 days. This water is completely transferred to the fine pores, explaining the increasing function of fine pores with wetting time. The water transfer from the large pores to the fine pores seems to be faster with an increase in temperature. However, this increase does not allow the capture of the initial water in the large pores, especially for W40. At 60°C, after one day of measurements, the transfer seems almost complete, while this necessary period is longer for lower temperatures.

The coefficient of water transfer from large to fine pores can be calculated using Eq. (5). This rate is dependent on the water distribution in the pores as shown in Fig. 6. This dependency on the ratio \( W_l / W_f \) can be approximated by a linear function as presented by Fig. 6. The phenomenological concept of this equation is that the pores or surfaces where the water redistribution occurs, and the large pores and the fine pores are connected, and it would be a function of the ratio of volume of the large and fine pores. Therefore, as a first order approximation, Eq. (5) is applied. A constant coefficient (the gradient) independent from the water distribution in pores of cement paste can be extracted from the linear fitting. this coefficient was named \( \beta \) in this paper.

\[
\alpha = \beta \frac{W_l}{W_f}
\]  

(5)

The coefficient \( \beta \) obtained for different temperatures and for both mixtures is presented as the slopes of lines in Fig. 6. For 20°C, \( \beta \) of W40 – 20°C is smaller than that of W55 – 20°C. This is likely due to the difference of the ratio of gel pores to fine pores, as shown in Fig. 4. However, at 60°C, the trend reverses. Furthermore, the values show a clear temperature dependency similar to water transport coefficients in concrete such as the diffusion coefficient and the permeability coefficient.

The change in diffusion with temperature can be ex-
pressed as Eq. (6), where the temperature dependency is explicitly shown (Jooss and Reinhardt 2002). The permeability can be expressed theoretically as function of water density $\rho$, the gravitational constant $g$, the specific surface area of the particles $\sigma$, the coefficient of viscosity $\eta$, and the porosity $\varepsilon$, as shown in Eq. (7) (Powers, 1979).

\begin{equation}
D = \text{cste} \left( \frac{T}{T_0} \right)^n
\end{equation}

This equation allows us to express the ratio of the permeability for two different temperatures as:

\begin{equation}
\frac{k_T}{k_0} = \frac{\rho_T \eta_T \varepsilon_T (1 - \varepsilon_T)}{\rho_0 \eta_0 \varepsilon_0 (1 - \varepsilon_0)}
\end{equation}

Fig. 5 The combined water components calculated based on the CPMG echo signal of W40 and W55 under 20°C, 40°C, and 60°C and the evaporable water content of W40 and W55 calculated based on the mass change under 20°C, 40°C, and 60°C.
According to Eq. (8), the influence of temperature on permeability can be separated into two parts. The first part concerns the density and viscosity of water. The second part is related to the nature of the material through the specific surface and porosity, which can vary with different mechanisms, such as the dilatation of the porous structure with temperature (Choinska et al. 2007) or the dynamic microstructure observed here. If the impact of the variation of the water properties according to temperature is considered, then permeability should at least double between 20°C and 60°C, as shown in Table 3. If it is assumed that the rate of water transfer is also influenced by the same parameters, then its value at 60°C should also be greater than twice its value at 20°C, which is the case for both compositions as presented in Table 3. The further increase beyond this estimated factor of two can then be related to the microstructural modification of the cement paste due to the temperature increase. This difference is higher in the case of W40 for which the microstructure is finer and should be more impacted by the water movement, especially when this motion accelerates with temperature. In addition, for the very narrow pores of cementitious materials, the Knudsen effect can take place with more frequent collisions of water molecules with the solid matrix as compared with their collisions with each other (Gawin et al. 1999).

4.2 Activation energy of the rate of exchange between large and fine pores

The Arrhenius plot for the rate of exchange between large and fine pores versus the reciprocal of the absolute temperature is presented in Fig. 7 for W40 and W55. The activation energy divided by the gas constant ($R = 8.314 \text{ J.K}^{-1}\text{.mol}^{-1}$) is the gradient of these curves. Thus, the activation energies for W40 and W55 are 36 kJ/mol and 35 kJ/mol, respectively, which are very similar values.

| T (°C) | $\rho$ (kg/m$^3$) | $\eta$ (mPa.s) | $\frac{\rho_T}{\rho_{20^\circ}}$ | $\frac{\eta_T}{\eta_{20^\circ}}$ | $\frac{(\rho_T/\rho_{20^\circ})(\eta_T/\eta_{20^\circ})}{1}$ |
|-------|-----------------|----------------|-----------------|-----------------|-------------------|
| 20°C  | 998.2           | 1.002          | 1               | 1               | 1                 |
| 40°C  | 992.2           | 0.6531         | 0.994           | 1.534           | 1.53              |
| 60°C  | 983.2           | 0.4658         | 0.985           | 2.151           | 2.12              |

**Table 3** Water properties calculated from 20°C to 40°C and then to 60°C.

![Fig. 6 Relationships between coefficient $\alpha$ and $W/W_l$ for water moving from large pores to fine pores.](image1)

![Fig. 7 Temperature dependence coefficient of $\beta$.](image2)
For comparison, the activation energy of diffusion can be calculated by Eq. (6), with its Arrhenius plot presented in Fig. 8. Based on this plot, the activation energy of the diffusion process in the studied temperature range is equal to 29 kJ/mol. The same approach can be adopted for the permeability process via Eq. (8). The Arrhenius plot of permeability linked to the water properties is also presented in Fig. 8. If no microstructural change is assumed (by assuming a constant specific surface and porosity), then the activation energy related to the permeability is equal to 14 kJ/mol. However, an additional activation energy should be added to this value, owing to the microstructural modification by considering the porosity and specific surface variations, especially since the difference in evaporable water at 26 days under different temperatures is still negligible, as shown in Fig. 4. By considering the porosity of the material corresponding to this amount of water, the porosity can be assumed to be almost constant for this temperature range. Thus, the activation energy of permeability due to porosity variation will be null and the only remaining source of this activation energy will be the variation of the specific surface.

The temperature dependency of the specific surface seems to be more important than that of the porosity as the term representing this dependency is squared in Eq. (8). However, for a similar material (white Portland cement, with water-to-cement ratio 0.55 and similar mineral composition, and from the same factory) studied in a previous publication (Maruyama et al. 2018), the measured specific surface variation according to the temperature was very small. Its corresponding activation energy calculated from the permeability from Eq. (8) will also be negligible (around 2 kJ/mol). Thus, the total activation energy of permeability in the materials used in this study should be slightly higher than 16 kJ/mol if the porosity variation due to temperature is also considered. Both water transport processes give lower values than those experimentally observed, which can be explained by additional microstructure evolution that is not considered in this theory. The microstructural reorganization may be the source of this observed difference, which requires energy to transform the interlayer pores back to gel pores under saturation.

For both mixtures, the curves are not perfectly linear and a double-slope shape can be observed in Fig. 7. This double-slope shape was also observed previously for the same temperature range under diffusion for ordinary Portland cement (cured for 28 and 90 days) and aluminous cement (Glover and Raak 1972). In addition, Drouet et al. (2015) described the temperature dependency of permeability as a non-Arrhenius behavior. Instead, to fit the behavior linearly, they suggested a double exponential function. However, in this case, a double-slope fitting can also be adopted for the four studied cements. In these two published studies, the temperature for which the curves have an inflection point is approximately 40°C, which is similar to the results of the present study. This difference occurs in parallel with the substantial increase of gel pore water at 60°C for both mixtures, as compared to the two other temperatures. For W40, this represents a significant change in microstructure from an equivalent quantity of water between interlayer and gel water to dominant gel pores. For the W55, due to the larger amount of initial gel pores, the classification between gel and interlayer pores was not affected while the gel pore proportion increases with temperature. Thus, this non-perfect linearity can be associated with the variation in the required energy to move water from large to fine pores and to reorganize the microstructure.

5. Conclusion

The water distributions in two different mixtures of white Portland cement paste were investigated through proton-nuclear-magnetic-resonance relaxometry. The water uptake test was performed at three different temperatures: 20°C, 40°C, and 60°C. The water present in four porosities (interlayer, gel, interhydrate, and capillary pores) was measured for the sealed condition and dried condition, and during the first twenty-six days of sorption. Based on the obtained results, the following conclusions can be drawn:

1. The interhydrate pores are quickly filled with water at the beginning of the sorption test before emptying into the finest porosities over time.
2. The movement of water from different pores to the gel pores increases with time and temperature.
3. The rate of water exchange between large pores (capillary pores and interhydrate pores) and fine pores (gel pores and interlayer spaces) was obtained, showing an increasing tendency with temperature.
4. The activation energy of 35 kJ/mol corresponding to water exchange between large and fine pores was similar for both studied compositions.
5. The activation energy obtained from the diffusion or permeability processes based on previous studies was inferior to the measured result. This difference can be
linked to the microstructural rearrangement observed experimentally, which is not considered in classical water transport theories.

(6) A double-slope curve was observed in the Arrhenius plots. The finest microstructure showed an important variation in the proportion of the gel and interlayer pores between the lowest two temperatures (20°C and 40°C) and the highest temperature (60°C), which can be linked to the variation in the necessary energy to move water between pores and to reorganize the microstructure.

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