

Summary

Title: Effect of elevated temperature on water uptake behavior in cement-based materials (セメント系材料の吸水挙動に及ぼす昇温の影響)

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In recent years, many problems such as premature deterioration and shrinkage cracking of concrete structures have been raised, and it has become an issue to extend the service life of buildings and to predict the future, and it is required to evaluate the performance such as strength and durability along the time axis. Cracks in concrete allow rainwater and salt to penetrate the concrete and accelerate the deterioration of the building. Cracks in concrete lead to a reduction in strength and Young's modulus, which are governed by factors such as aggregate, cement hardener and voids. Among these, chemical changes in the cement hardener and physical changes in the voids are the most important factors. Therefore, it is important to measure the pore structure of concrete, mortar and cement paste in order to understand their physical properties and durability. In addition, concrete structures in real environments are subjected to all kinds of changes. It is necessary to understand the changes in the hardened cement under such realistic conditions, such as drying, which is a cause of cracking of concrete. Therefore, it is necessary to understand the behavior of water and the change of porosity in concrete under various conditions such as drying and high temperature.

A detailed literature review about the structure of Calcium Silicate Hydrate (C-S-H) presents in cement pastes have a great variability in terms of composition, structure, and microstructure. All this, together with the fact that the C-S-H has an amorphous nature, means that its structure is not well known. There has been a succession of experimental work was done at developing a structural model of the hydrated phases of cement. The models that attempt to explain the structure of C-S-H by :- Crystalline models, and by Meso-scale models. Based on scientific and technological development gradually made it possible to study this compound in greater depth through the application of new techniques.

In this study, $^1\text{H-NMR}$ relaxometry is an established powerful technique for non-invasive and non-destructive characterization of pore size distribution and pore water interaction in cement-based materials. $^1\text{H-NMR}$ experiments have been proven to be quantitative. The measured CPMG were analyzed with ILT algorithm to obtain T_2 distribution. The water uptake test was performed at three different temperatures (20 °C, 40 °C and 60 °C). The water present in four peaks and the ratio of each peak to the intensity were used to evaluate the quantities of interlayer

water, gel pore water, interhydrate pore water and capillary pore water was measured for the sealed condition, dried condition and during the 26 days of water absorption process.

The evaporable water for different samples was measured with a balance in different conditions. The mass evolutions given by the balance and that obtained by $^1\text{H-NMR}$ signal being generally in the same range confirms that all the water is captured by $^1\text{H-NMR}$ relaxometry. A high evaporable water content was observed for W55 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.

During the water absorption process, the interhydrate pores are quickly filled with water at the beginning of the sorption test before emptying into the finest porosities over time. The distribution of water from different pores to the gel pores increases with time and temperature. The water in the cement paste can be divided into two categories, the water in either fine pores or large pores. Where fine pores is the sum of (interlayer water + gel pore water) and where large pores is the sum of (interhydrate pore water + Capillary pore water). Based on the NMR signal, the 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, the $60\text{ }^\circ\text{C}/20\text{ }^\circ\text{C}$ and $40\text{ }^\circ\text{C}/20\text{ }^\circ\text{C}$ signal ratios were 0.880 and 0.936, respectively, while the obtained CPMG data was normalized by the data at the $20\text{ }^\circ\text{C}$ condition. It is also assumed that the T_2 values at different temperatures are not affected by the temperature of the sample. The rate of water redistribution between large pores and fine pores can be obtained and showing an increasing tendency with temperature. The activation energy for W40 and W55 are 36KJ/mol and 35KJ/mol corresponding to water exchange between large and fine pores was similar for both studied compositions. The activation energy obtained from the diffusion or permeability processes based on the 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. A double slope 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 temperatures ($20\text{ }^\circ\text{C}$ and $40\text{ }^\circ\text{C}$) and the higher temperature ($60\text{ }^\circ\text{C}$), which can be linked to the variation in the necessary energy to move water between pores and to reorganize the microstructure.

The fast diffusion relaxation model links the T_2 relaxation time. 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 $1.73\pm 0.08\text{ nm}$ for W40 and approximately $2.07\pm 0.11\text{ nm}$ for W55. Under $105\text{ }^\circ\text{C}$ 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 2.34 ± 0.33 nm, respectively, at 40 °C and to 2.00 ± 0.19 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 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 (7.31 ± 0.00 nm) at 60 °C. For interhydrate and capillary pores, more fluctuation is observed with temperature, which can be explained by the signal to noise ratio and lower number of detected pores as compared to the finest pores.

X-ray computed radiography is a non-destructive method, and to analyze the behavior of liquid water movement in mortar specimens. The Washburn's equation which is a theoretical equation of water absorption behavior in a circular tube driven by capillary tension, is introduced as a water absorption process applicable to cement-based materials. In the present study, it was confirmed that the behavior was in accordance with the Washburn's equation. Based on the X-CR imaging, the liquid water distribution could be visualized by subtracting the difference in the images between the transmitted image at each water absorption process and the transmitted image at drying as a background image. By comparing the changes in the luminance values of the transmitted image in the direction of water absorption with the luminance value of the transmitted image during drying, the distance of liquid water penetration was derived. It was confirmed that the distance of water penetration and the amount of cumulative water absorption were approximately linearly related to the square root of time and behaved in accordance with Washburn's equation, which indicated that the data obtained by non-destructive measurement using X-CR observation was valid and significant experimental method. X-CR was used to measure the sorptivity of mortar containing different cement and aggregate types under two different temperature conditions (20 °C and 60 °C). The results were numerically evaluated using a simplified finite differential method, which considered microstructural changes after water uptake and the resultant changes in the water transfer coefficient. The sorptivity measurements showed that water transport displayed anomalous behavior; the relationship between the penetration depth or total absorbed volume of water and the square root of exposure time deviated from a linear relationship and became nonlinear. The trend was bimodal, and the second slope appears after a certain hour of exposed time, which is necessary to show the rearrangement of C-S-H structure. Mortar containing fly ash (FAC mortar) had a lower sorptivity than that of mortar

containing ordinary Portland cement (OPC mortar) under the same volumetric mixture proportions. One possible explanation is that the morphology of calcium silicate hydrate (C-S-H) is affected by the calcium-silicate ratio. The behavior of water in the OPC mortar was more anomalous than in FAC mortar. At higher temperatures, the first slope is larger, while the second slope is smaller. The second slope cannot be explained only by changes in the surface tension and viscosity of the pore solution; C-S-H structure rearrangement may be the dominant factor for the slope change at elevated temperatures.