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Water Uptake in OPC and FAC Mortars under Different Temperature Conditions

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Abstract

This experimental and numerical study aims to evaluate the penetration depth of contaminated water in the concrete structures involved in the Fukushima Daiichi nuclear powerplant. The influence of the mortar mixture on water absorption was investigated by varying the composition: mortars containing aggregates from river sand and crushed limestone sand were compared, and 15% of the cement in the mixture was substituted with fly ash. The effect of temperature in nuclear conditions is also significant; therefore, water uptake at temperatures of 20 and 60°C was considered. Finally, pre-drying conditions were studied by drying the sample at two different conditions: at 105°C and at 40% RH (relative humidity) and 20°C. Water uptake was monitored using x-ray computed radiography in combination with mass measurements. In all cases, anomalous sorption, or a nonlinear relationship between penetration depth and the square root of exposure time was observed, with the sorption curves showing bimodal behavior. The aggregate type had no significant effect on the water uptake results. However, the samples containing fly ash clearly had lower water uptake rates, which can be explained by the differences in the calcium silicate hydrate (C-S-H) structures. With increasing temperature, the penetration was slightly accelerated at the beginning of the experiment, with the rate of penetration then decreasing rapidly. The densification of C-S-H at higher temperatures could contribute to this phenomenon. Microstructural rearrangements can also explain why the highest uptake rates occurred for samples that were exposed to severe drying conditions (105°C). The experimental results were consistent when the microstructural rearrangement was considered, further confirming these conclusions.

1. Introduction

Following the accident at the Fukushima Daiichi Nuclear Power Plant (FDNPP), a plan for decommissioning the plant must include an estimation of the level of contamination in the concrete due to the enormous quantity

of material. As a part of the decommissioning, the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), conducted a project between January 2018 and March 2020 called “Analysis of radionuclide contamination mechanisms of concrete and the estimation of contamination distribution at the Fukushima Daiichi nuclear power station.” To assess the level of contamination in concrete structures accurately, it is important to consider water transport and microstructural changes within the material. The concrete in the Fukushima NPP buildings has a relatively low moisture content after many years of service (Ryměš *et al.* 2019; Maruyama *et al.* 2021). After the accident, part of the concrete surface was exposed to heat and drying conditions, then was subsequently exposed to seawater and contaminated water. Additionally, water was continuously supplied to cool the fuel, and liquid water continued to pool in the lower portions of the buildings. The volume of water used as a coolant has gradually decreased since the accident. An analysis of the history of exposure and the boundary conditions for the concrete members will be presented in a companion paper.

As a first step in the contamination estimation procedure, the water uptake behavior of materials similar to those used in the Fukushima Daiichi NPP buildings is studied. It should be mentioned that shrinkage-induced visible cracks as well as cracks around aggregate has a large influence on the moisture/liquid water transport in concrete, however, as a first step research program, sev-

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Table 1 Example mixture proportions for concrete used in the Fukushima Daiichi Nuclear Power Plant buildings.

	W/C	S/C	Unit amount (kg/m ³)				AE agent
			W	C	S	G	
Concrete	0.55	2.39	182	330	790	1000	99 mL

W: unit water content, C: unit cement content, S: unit sand (fine aggregate) content, G: unit gravel (coarse aggregate) content.

Table 2 Material properties of the mixture components.

Material	Notation	Information
Cement	OPC	Ordinary Portland cement (density: 3.16 g/cm ³ , specific surface area: 3140 cm ² /g)
Fly Ash	FA	JIS Class II (density: 2.37 g/cm ³ , specific surface area: 4210 cm ² /g) (Class C by ASTM C 618)
Fine aggregate (maximum diameter 2.5 mm)	LS	Crushed limestone sand (excluding fine particles less than 0.15 mm in diameter)
	RS	On-site aggregate (including river sand and fine particles)
Admixture agent	AE	From diluted pulverized Vinsol resin (Yamaso Chemical Co. Ltd.)

Table 3 Mixture composition of the mortar specimens.

Mixture ID	Water to binder ratio	FA (%)	Unit amount (kg/m ³)					AE agent (mL)	
			Water	Cement		LS	RS		
				OPC	FA				
OPC-LS	0.55	0	182	330	-	790	-	86	
FAC-LS		15		280.5	49.5	790	-	255	
FAC-RS						-	790	123	

Notes: (1) Added gypsum and adjusted the total SO₃ content in the powder to 2.5%; (2) The AE agent was used by diluting Vinsol resin (Yamuna Chemical Co., Ltd.) one-hundred times. The amount of AE agent added represents the targeted amount of air (7.0 ± 1.0%).

Table 4 Chemical composition as determined by XRF analysis (mass %).

Cement	LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	SrO	Total
OPC	2.26	20.54	5.18	2.92	64.30	0.90	2.04	0.35	0.32	0.31	0.57	0.08	0.05	99.82
FA	2.41	56.23	30.89	3.05	1.66	0.92	0.23	0.36	1.24	1.67	0.49	0.02	—	99.17

Table 5 Mineral composition of the OPC cement as determined by XRD/Rietveld analysis (mass %).

C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Periclase	Basanite	Gypsum	Calcite	Total
50.35 ± 1.22	23.27 ± 2.07	8.79 ± 0.30	10.10 ± 0.37	0.38 ± 0.12	1.90 ± 0.155	0.16 ± 0.04	5.01 ± 0.39	99.96

eral factors, which are originated from the characteristics of materials used in the Fukushima Daiichi NPP buildings, including temperature, drying conditions, and mortar composition are investigated. Furthermore, to understand the anomalous water transport behavior that was previously reported (Martys and Ferraris 1997; Taylor *et al.* 1999; Hall 2007, 2019; Biagioni *et al.* 2012; Alderete *et al.* 2019; Wu *et al.* 2019; McDonald *et al.* 2020; Zhang and Angst 2020), a simplified numerical analysis is conducted. The behavior is investigated by considering dynamic microstructural changes in calcium silicate hydrate (C-S-H) (Muller *et al.* 2013; Gajewicz *et al.* 2016; Zhou *et al.* 2017; Maruyama *et al.* 2019; Kiran *et al.* 2020), a major group of hydrates in cement-based materials that is influenced by variations in temperature.

2. Experiment

2.1 Materials and curing conditions of the mortar specimens

The materials for this experiment were fabricated ac-

cording to the construction records from the NPP at the Fukushima Daiichi site (Kaburagi 1969). One mixture proportion, shown in **Table 1**, was selected from the records. Class II fly ash powder meeting the Japanese Industrial Standard Code (JIS A-6201) was used. The material properties and mixture proportions for the samples used in this study are shown in **Table 2** and **Table 3**, respectively.

The chemical composition of the ordinary Portland cement and fly ash powder as determined by x-ray fluorescence (XRF) is shown in **Table 4**. The phase composition of the powdered samples of raw ordinary Portland cement and natural fly ash was determined using x-ray diffraction (XRD) (D8 Advance, Bruker AXS) and Rietveld analysis software (TOPAS ver. 4.2 developed by Bruker AXS), as shown in **Table 5** and **Table 6**, respectively.

Table 7 shows the chemical composition of the fine aggregates. The minerals, which were identified in the samples using polarized micrography and XRD measurements, are listed in **Table 8**.

Table 6 Mineral composition of the fly ash as determined by XRD/Rietveld analysis (mass %).

Quartz	Mullite	Magnetite	Hematite	Calcite	Rutile	Glass	Total
8.71 ± 0.32	26.42 ± 0.54	0.11 ± 0.05	0.27 ± 0.06	0.64 ± 0.14	0.33 ± 0.26	63.49 ± 1.03	99.97

Table 7 Chemical composition of the fine aggregates as determined by XRF (mass).

	LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Total
RS	1.03	79.51	8.75	3.30	1.85	1.45	0.01	1.86	1.69	0.35	0.05	0.10	99.95
LS	41.66	5.35	0.72	0.26	47.03	4.57	0.02	0.04	0.15	0.03	0.03	0.00	99.86

Table 8 Minerals observed in the fine aggregates from the micrograph and XRD/Rietveld analysis.

	Quartz	Plagioclase	Orthoclase	Chlorite	Mica	Amphibole	Calcite	Dolomite
RS	x	x	x	x	x	x		
LS							x	x

Note: 'x' indicates that the target phase was confirmed by XRD analysis.

The mortar was mixed with a Hobart mixer. Each batch had a total mixture volume of 4 liters. The mortar was placed in a mold with a cross-sectional area of $50 \times 50 \text{ mm}^2$. The specimens were cured at 40°C in moist condition (100% RH) for three months. Then, they were cut into $20 \times 20 \times 50 \text{ mm}^3$ blocks using a diamond precision saw. This accelerated curing at 40°C was applied in order to obtain the sufficient degree of hydration (the degree of reaction of the glass phase in FA was about 50% (selective dissolution method) and degree of hydration of OPC was about 91% (XRD/Rietveld analysis) in order to obtain the similar reacted condition to that in aged structure.

2.2 Water absorption test method

After the sample was homogeneously dried at 105°C or at 20°C and approximately 40% RH, all surfaces except for one, with dimensions of $20 \times 20 \text{ mm}$, were covered with aluminum adhesive tape. For the drying condition at $105 \pm 2^\circ\text{C}$, a heating chamber was used. Each specimen was inserted in a glass bottle, and a silicon tube connected the glass bottle to a gas washing bottle placed outside of the heating chamber. The gas washing bottle contained calcium hydroxide aggregates, which prevented the carbonation of the specimens. The drying process took

approximately one day. For the condition at approximately 40% RH and 20°C , a saturated salt solution [solutions containing pure NaI can be used to maintain an RH of approximately 39.65% at 25°C (Greenspan *et al.* 1977)] was used to maintain a constant relative humidity. The drying period took 93 days, ensuring a quasi-equilibrium condition [0.01%/day according to (Wu *et al.* 2019)] for all samples. This 105°C was selected as the reference that is the most commonly used, and 20°C and 40% RH was selected since this drying state is similar to the drying condition on the surface of thick concrete walls in nuclear power plants [an estimation was made based on references (Rymes *et al.* 2019; Maruyama *et al.* 2021)].

As shown in Fig. 1, a tap water absorption test was conducted from the bottom of the specimen. The temperature of the water and the ambient environment was controlled at the target temperatures, $20 \pm 2^\circ\text{C}$ or $60 \pm 5^\circ\text{C}$. The specimen and a water reservoir were placed inside the x-ray CT scanner. During the twenty-four hour water absorption experiment, transmission images of the sample were taken intermittently. Immediately after transmission imaging, the specimen was removed, and the mass was measured using an electronic balance. For measurements at 60°C , the water absorption test was

(a) Schematic representation of the water adsorption

(b) Setup in x-ray radiography equipment

Fig. 1 Schematic representation of the water absorption process in a controlled temperature chamber (a) and experimental setup for x-ray radiography measurement (b).

performed in a 60°C heating chamber. The specimen was removed from the furnace for transmission imaging, and then the water absorption test was restarted in the furnace. It was expected that the specimen's temperature would decrease during the transparent imaging. However, it took approximately 150 seconds to remove the sample from the furnace, perform x-ray radiography, and return it to the furnace. As the interval between imaging was several hours, it was determined that the sample temperature dropped by approximately 5°C during this 150 second interval. The samples were labeled according to their mixture identity, drying condition, and experimental temperature. For example, an OPC-LS specimen dried at 105°C and measured at 20°C was labeled "OPC-LS-105C-20".

2.3 X-ray imaging process

X-ray imaging techniques have several advantages for capturing the water absorption behavior of cementitious materials. When the specimen is exposed to air during the water absorption test, the water penetration depth shows a concave-shaped distribution inside, and the results observed at the surface are not sufficient to evaluate the penetration depth. Secondly, from the x-ray attenuation, the mass difference can be estimated using a calibration curve from the obtained image. It should be noted that there is a limit to the thickness (or size) of the sample depending on the x-ray source and detector.

For x-ray computed radiography (CR) observations, the inspeXio SMX-100 CT system (Shimadzu Corporation) was used. The maximum tube voltage and current in this instrument are 100 kV and 120 μ A, respectively. The Feldkamp, Daci, Kress (FDK) method, a cone-beam reconstruction method, was used as the algorithm for image reconstruction (Feldkamp 1984). In this study, the tube voltage was 100 kV, the tube current was 110 μ A, the SDD (distance from the x-ray focus to the detector) was 500 mm, the SRD (distance from the x-ray focus to

the sample) was 350 mm, and the number of feed lines was four. Ten measurements were conducted for each sample, and radiography was performed using a Cu filter with a thickness of 0.4 mm. To convert the brightness of the transmitted image to useable measurement values, iron (3 mm thick) and quartz (16 mm thick) were used as references. The grayscale range of the resultant image was normalized, and the spatial resolution of the picture was 0.0176 mm/pixel.

As shown in **Fig. 2**, the moisture content was visualized by subtracting the initial image (before water absorption) from the x-ray transmission image taken six hours into the water absorption experiment. It is important to subtract the background from the transmission image for each water absorption process to determine the penetration depth. Using this method and the differences in gray scale values in the images, the infiltration depth of the liquid water and the total volume of absorbed water in each sample was calculated. The open-source image analysis software ImageJ (Schneider *et al.* 2012) was used for processing and grayscale digitization. x-ray computed radiography (X-CR) was used to image the water absorption for 24 hours at 20°C and 60°C respectively. One sample per once condition was measured in this experiment.

2.4 Quantification of water

The attenuation behavior of the x-rays could be described using the Beer-Lambert law. The water absorption levels were quantified from the x-ray radiography images using process evaluated by Roels and Carmeliet (2006). The amount of water absorbed for each pixel (ΔC_w) can be calculated as,

$$\Delta C_w * \mu_w = -\frac{\rho_w}{d} \ln \frac{I_{wet}}{I_{dry}} \quad (1)$$

where I_{wet} is the attenuated x-ray intensity through a

Fig. 2 X-ray transmission images before and after six hours of water absorption. The width of the image is about 2 cm.

wet mortar specimen, I_{dry} is the attenuated x-ray intensity through a dried mortar specimen, ρ_w is the density of water (g/cm^3), d is the thickness of water (cm), and μ_w is the nominal attenuation coefficient of water in the mortar (cm^{-1}).

For calculating the water absorption from the discretized gray scale values from the x-ray CR images, Eq. (1) was used with $\rho_w = 1.00 \text{ g/cm}^3$. The total mass change due to the water evaporation should be correlated to the integration of ΔC_w for all pixels. Based on the experiment, μ_w was evaluated by fitting the experimental data to correlate the change in mass. As shown in **Fig. 3**, μ_w was determined to be 0.0185 cm^{-1} in our measurement system.

3. Experimental results

The representative results for FAC-LS-105C-20 are shown in **Fig. 4**. The dark area represents the region in which the water was absorbed in the mortar specimen.

Fig. 3 Relationship between the change in mass and the change in brightness value in the x-ray transmission images.

This figure can be used to evaluate the relationship between average brightness and distance from water absorption surface. The results for OPC-LS-105C-20, FAC-LS-105C-20, and FAC-RS-105C-20 are summarized in **Fig. 5**. The change in the moisture distribution was quantitatively analyzed using these figures. Additionally, this data was used to calculate the penetration depth and the volume of water absorbed in the sample. The results for OPC-LS-105C-20 are shown in **Fig. 6**. The absorbed water values were normalized per unit of projected area. As each specimen had dimensions of $20 \times 20 \times 50 \text{ mm}^3$, the total absorbed water can be calculated by a factor of 1000 based on the sum of difference of normalized gray values. **Figure 6** shows the anomalous behavior of water adsorbed in cement-based materials, a phenomenon characterized by water absorption behavior that deviates from the linear relationship between water penetration depth or volume of water absorbed and the square root of time. According to these results, the penetration depth began to deviate from the linear curve (denoted as point A) at approximately 400 minutes (at around $20 \text{ min}^{0.5}$ in the x-axis of **Fig. 6**) after the first contact with water, while the water absorption amount began its deviation (denoted as point B) at approximately 10 hours (around $25 \text{ min}^{0.5}$ in the x-axis of **Fig. 6**). After approximately 15 hours (around $30 \text{ min}^{0.5}$ in the x-axis of **Fig. 6**), more significant reduction of water absorption was confirmed. As the experiment proceeded, maximum water amount is slightly increased as the depth is increased, consequently, between the timings of point A and point B, the discrepancy between penetration depth and the water absorption amount was confirmed.

After the point B where the corresponding depth is from 15 mm to 22 mm, the maximum water absorption starts to decrease and the distribution of water (as a function of the distance from the water contact surface) near the penetration depth became broad, and then the significant reduction of the rate of absorption was observed in **Fig. 6**. Currently mechanism of the slight in-

Fig. 4 Visualization of water penetration in mortar specimen. The width of image is about 2 cm.

crease of the maximum water adsorption at the depth ranging from 0 to 15–22 mm was not clear, and one possible explanation is an artifact due to x-ray scattering from the water at the bottom. On the contrary, after the

point B, the trend of decrease in the maximum absorption as the increase of penetration depth and broadening of the water distribution near the penetration depth can be explained by the connectivity of pores. If there is a large

Fig. 5 Results of the x-ray computed radiography (average brightness value) for the water absorption, in which water at 20°C was absorbed from the bottom surface of the mortar specimens dried at 105°C.

Fig. 6 Penetration depth and cumulative water content per unit area of OPC-LS-105C-20. The points represent experimental data, while the solid lines represent the sorptivity of specimens at the beginning of experiment, determined by the first several experimental data points.

pore in which the liquid water cannot transport and fill in, the maximum of water will be decreased at the same depth of the large pore. As a result, the rate of water absorption is decreased against the square root of time, while the penetration depth can keep the linear relationship against the square root of time. In summary, in **Fig. 5**, there are two anomalies of moisture transport. One is the inflection point of the penetration depth as a function of the square root of time (point A), and the deviation between the penetration depth and the water absorption against the square root of time. Hereafter point A is mainly discussed.

The experimental results are summarized in **Fig. 7**. **Figure 7(a)** shows the effect of cement type on the rate of water absorption. At the beginning of the water absorption experiments, the water absorption coefficient rate (sorptionity, expressed in $\text{mm}/\text{min}^{0.5}$) of the FAC mortar was approximately 70% that of OPC mortar. Interestingly, the anomalous trend was much stronger for OPC mortar than for FAC mortar [see **Fig. 8(a)**]; FAC showed a more linear trend as a function of the square root of exposure time. These trends are consistent with those

reported in previous studies (Gopalan 1996; Tasdemir 2003; Leung *et al.* 2016; Hatungimana *et al.* 2019; Jena and Panda 2021). The morphology of calcium silicate hydrate (C-S-H), a major hydrate in cement-based materials and a source of strength in concrete, can be changed by changing the calcium silicate (Ca/Si) atomic ratios (Richardson 1999, 2004; Richardson *et al.* 2010). C-S-H with a lower Ca/Si ratio has a foil-like structure, which may be a major reason for its lower diffusion coefficient and lower sorptivity, being formed by the pozzolanic reaction. **Figure 7(b)** shows a little effect of rock type on the sorptivity rate. Two possible factors that could affect the sorptivity rate. One is the interfacial transition zone, which can be changed by the reaction of cement hydrates and rock-forming minerals, as calcium aluminate hydrates can be formed on the surface of calcite, while the portlandite can be the major phase on the quartz (Ping *et al.* 1991). It should be noted that the interfacial transition zone does have significant impact on mass transfer in concrete rather than the microcracks caused by pre-drying condition (Wong *et al.* 2009). The other is the presence of clay minerals (but only few

Fig. 7 Penetration depth of water in the mortar over time: (a) impact of cement type (OPC vs. FAC), (b) impact of aggregate type (limestone vs. sandstone containing clay minerals), (c) impact of temperature on OPC mortar (20°C and 60°C), (d) impact of temperature on FAC mortar (20°C and 60°C), (e) impact of pre-drying conditions on OPC mortar (drying at 105°C or at 20°C and 40% RH), and (f) impact of pre-drying conditions on FAC mortar (drying at 105°C or at 20°C and 40% RH). The solid lines shown in (c) represent the sorptivity slope at the beginning of the experiments.

Table 9 Measured sorptivity (mm/min^{0.5}).

	OPC-LS-105C-20	FAC-LS-105C-20	FAC-RS-105C-20	OPC-LS-105C-60	FAC-LS-105C-60	FAC-RS-105C-60	OPC-LS-40RH-20	FAC-LS-40RH-20
Initial*	1.34	0.94	0.92	1.67	1.09	1.076	0.87	0.54
After 1-day**	1.17	0.89	0.86	0.84	0.73	0.73	0.71	0.38

*: the initial sorptivity was calculated by the linear fitting of the data within 240 minutes after water contact.

**: the sorptivity after 1 day is calculated as a tangent between origin and the data at 24 hours after water contact.

percent) in sand, which can absorb the water. From **Fig. 7(b)**, it is concluded that these two factors were not significant for the aggregate used in the Fukushima Daiichi plant.

Temperature has a significant effect on the sorptivity, as confirmed in **Fig. 7(c)**. At the beginning of the water sorption process, the sorptivity of OPC-LS-105C-60 was approximately 35% higher than that of OPC-LS-105C-20. However, the anomalous behavior of OPC-LS-105C-60 is much greater than that of OPC-LS-105C-20, and after 24 hours, the penetration depth in OPC-LS-105C-60 was 28% smaller than in OPC-LS-105C-20.

All the measured sorptivity was summarized in **Table 9**. Based on the Washburn equation (Washburn 1921), the penetration depth can be evaluated as,

$$L = \sqrt{(\gamma r \cos \theta / 2\mu) \cdot t} \quad (2)$$

where L is the penetration depth, γ is the surface tension (N/m), μ is viscosity (Pa·s), r is the radius of the pore (m), and t is the exposure time (s). When the temperature is changed, the viscosity and the surface tension of the pore solution change due to the thermodynamic behavior of water molecules. Additionally, the radius of pore changes due to thermal deformation in the solid components of the mortar structure. The structural deformation in the mortar contributed to a change of the order of 10^{-4} . The surface tension of water is 72.75 and 66.17 N/m at 20°C and 60°C, respectively, and the viscosity of water is 1.002 and 0.467 (mPa·s) at 20°C and

60°C, respectively. The ratio of $\sqrt{\gamma/\mu}$ at 60°C to that at 20°C was 1.40; this value is a bit larger than the experimental value of 1.16 to 1.25, but it is reasonably concluded that this is the major factor of the change in the initial sorptivity (the first slope of the sorptivity after water contact, less than 240 minutes). The viscosity and the surface tension of the pore solution are affected by ion concentration. The first-order estimation did not consider concentration; however, the sorptivity could be roughly evaluated by considering the changes in surface tension and viscosity of pure water by using a factor of 0.5.

The FAC specimens also showed stronger anomalous behavior at higher temperatures. The penetration depth of FAC-RS-105C-60 after twenty-four hours was 15% smaller than that of FAC-RS-105C-20, as shown in **Fig. 7(d)**. These results show trends that are consistent with those for OPC mortar.

For the mild drying process at 40% RH, the sorptivity rate decreased, as confirmed in **Figs. 7(e) and (f)**. It is found that the anomaly appeared much earlier when mortars were pre-dried at 40% RH, as shown in **Fig. 8(b)**.

The anomalous behavior of water absorption in cement-based materials has been discussed in the literature for more than twenty years (Martys and Ferraris 1997; Hall 2007). The possible mechanisms for this behavior include hydration, cement hydrate precipitation, inhomogeneous micro-cracking in the specimen from the pre-drying process, concrete swelling, and dynamic microstructural behaviors resulting from the colloidal na-

Fig. 8 Comparisons of anomalous behavior trends for (a) OPC mortar and FAC mortar and (b) pre-drying conditions at 105°C and at 40% RH at 20°C for OPC mortar.

ture of C-S-H (Saeidpour and Wadsö 2015, 2016a, 2016b; Wu *et al.* 2015, 2019; Gajewicz *et al.* 2016; Zhou *et al.* 2017; Alderete *et al.* 2019; McDonald *et al.* 2020; Zhang and Angst 2020). In addition, one may think that the 5-surface sealed condition will create air entrapment inside the specimen and a back-pressure cause the change in rate of penetration. This is a possibility that the authors cannot deny. However, if this is the dominant mechanism, the inflection point shown in **Fig. 7** should have occurred at the similar penetration depth rather than the similar elapsed time.

In a companion paper, Kiran *et al.* (2020) showed that the water exchange from large pores to fine pores in different temperature conditions could be monitored by ^1H -NMR relaxometry. These results could be attributed to dynamic microstructural changes in C-S-H during water absorption. If both sorption anomalies in OPC mortar and FAC mortar mainly occur from dynamic structural changes in C-S-H and local water exchange from large pores to fine pores, the difference in behaviors between the two mortars can be explained by the morphology of C-S-H. The FAC mortar contains C-S-H with a lower Ca/Si ratio; as a result, the rate of moisture transport decreases. The lower sorptivity of FAC mortar is evidence that these C-S-H characteristics affect adsorption in the mortars. This macroscopic behavior should also affect the local water exchange from larger pores to fine pores since the foil-like shape of C-S-H increases the material's tortuosity. The impact of C-S-H morphology is a major factor that determines the sorptivity of mortar for specimens with similar water to binder ratios and aggregate contents. At higher temperatures, ^1H -NMR relaxometry confirms the rapid water exchange between large pores and fine pores. After the mortar is exposed to water, the C-S-H in the mortar near the water contact surface begins to expand, resulting in the rapid closure of the larger pores. Thus, as the larger pores rapidly close, the channels that carry large volumes of water into the mortar collapse. Thus, this is the mechanism for the strong and rapid anomalous behavior that occurred at higher temperature conditions. When the pre-drying conditions were incomplete and water remained in the fine pores, the number and the size of pores in the final specimen were smaller than in the mortars exposed to the more severe pre-drying condition at 105°C . Consequently, the water penetration rate decreased. In addition, the deviation (anomaly) in the specimens dried at 40% RH began much earlier than for specimens pre-dried at 105°C , as the larger pores closed faster when water was already present in the C-S-H.

The pre-drying procedure could also be the cause of the cracking of the specimens (Wong *et al.* 2009; Maruyama *et al.* 2014; Wu *et al.* 2015, 2017). The shrinkage of the hardened cement paste in the mortar was much larger than that of the fine aggregate, which inhibited the shrinkage and caused the cracking of the hardened cement paste in the mortar specimens. It is also possible that the hardened cement paste expands due to the ex-

pansion of the C-S-H agglomeration structure after contact with water; as discussed by Alderete *et al.* (2019), the expansion of the C-S-H agglomeration structure reduces the widths of micro-cracks around the fine aggregates. In the present experiment, the anomaly is still controlled by the nature of C-S-H, since the process of the narrowing the width of micro-cracks is always associated with the expansion of the C-S-H agglomeration structure.

Therefore, it is concluded that the anomalous sorptivity of water in cement-based materials could be qualitatively explained by the nature of C-S-H. This conclusion is consistent with a recent discussion by McDonald *et al.* (2020).

4. Numerical analysis

4.1 Background and modeling

As discussed in Section 3, the anomalous water sorption in cement-based materials can be explained by the colloidal nature of C-S-H. In this section, the anomalous behavior associated with microstructural changes and temperature is discussed. To explain these phenomena, a simple numerical moisture transport model is introduced.

4.1.1 Local moisture water exchange from larger pores to fine pores

In a previous study (Kiran *et al.* 2020), the local water exchange between larger pores and fine pores was modeled by Eq. (3),

$$\frac{\partial W_F}{\partial t} = \alpha W_L, \quad \alpha = \beta(W_L / W_F) \quad (3)$$

where W_F is the water in fine pores (in the interlayer spaces and gel pores in hardened cement paste) (g/g-solid), W_L is the water in large pores (interhydrate pores and capillary pores) (g/g-solid), α and β are coefficients representing the rate of moisture transport from large pores to fine pores (/s), and t is time. The total water content, W (g/g-solid), can be determined according by Eq. (4).

$$W_L + W_F = W \quad (4)$$

4.1.2 Moisture transport

Sakata (1983) experimentally determined that the water diffusion coefficient in concrete is a function of water content and proposed a simple model. Based on their model, Eq. (5) below was applied to this study:

$$\begin{cases} R \geq 0.8: K(R) = K_s \\ R < 0.8: K(R) = K_o + \frac{K_s - K_o}{1 + \left(\frac{0.8 - R}{0.8 - R_c}\right)^n} + \frac{K_s - K_o}{1 + \left(\frac{0.8}{0.8 - R_c}\right)^n} \cdot (R - 0.8) \end{cases} \quad (5)$$

where $K(R)$ is the moisture transfer coefficient (cm^2/s), K_o is the moisture transfer coefficient in a sample in its saturated condition (cm^2/s), R_c is the relative moisture

Table 10 Parameters for the numerical model, where $K_{F,20}$ and $K_{L,20}$ are water transfer coefficients in fine pores and large pores at 20°C, respectively. For calculations at 60°C, a factor of 1.4 can be applied.

Parameters	20°C	60°C	Additional comments
R_c	0.70	0.70	Fitted
n	0.28	0.28	Sakata (1983)
β (/day)	0.5	3.5	Kiran <i>et al.</i> (2020)
$K_{F,20}$ (cm ² /day)	2.8	1.2	$\frac{K_{F,60}}{K_{F,20}} = 1.40$
$K_{L,20}$ (cm ² /day)	100.0	200	$\frac{K_{L,60}}{K_{L,20}} = 1.40$

content at the inflection point, R is the relative water content (water content per the maximum water capacity, in g/g-solid), and n is an experimental constant. An example of the application of Eq. (5) in this study is shown in Fig. 9.

Additionally, changes in the microstructure can also be incorporated with the moisture transfer coefficient. The following equation according to McDonald *et al.* (2020) was adopted,

$$K_s = \frac{1}{\frac{R_F}{K_F} + \frac{(1-R_F)}{K_L}} \quad (6)$$

where K_F is the moisture transfer coefficient in fine pores (cm²/s), K_L is the moisture transfer coefficient in large pores (cm²/s), and R_F is the relative water content in fine pores (W_L / W_o , where W_o is the maximum water content).

4.2 Results and discussion

The parameters used in the calculations are summarized in Table 10. The calculation was performed using an implicit finite differential method with an incremental time step of 0.1 hours and a spatial span of 1 mm. The calculation results are compared with the experimental results in Fig. 10. The general trends observed experimentally are well reproduced by the simplified model.

Fig. 9 Example of the function determined by Eq. (5). In the calculation process, the maximum value changes with time due to changes in the microstructure.

In the present modeling, an inconsistency in the values for $K_{F,20}$ and $K_{L,20}$ can be observed, which represents the moisture transfer coefficients in fine pores and large pores, respectively, at 20°C. This discrepancy appears to be inappropriate. However, several reports have shown that the C-S-H packing density, interlayer spacing, and the microstructures change with temperature (Gallucci *et al.* 2013; Bahafid *et al.* 2017; Gajewicz-Jaromin *et al.* 2019; Maruyama and Ryměš 2019). According to these studies, the interlayer spacing for specimens at 10°C is 35% larger than that at 60°C, and samples at 60°C were associated with increased pore size (capillary and interhydrate pores). It is quite possible that the apparent water transfer coefficient in fine pores decreases due to narrowed necking pores and increased viscosity, while the apparent water transfer coefficient in large pores is increased due to the greater pore width and connectivity. Since these trends could only be qualitatively observed, further validation in a future study is recommended. In mortar, the difference between the thermal expansion coefficient of hardened cement paste and aggregate could affect the water transport near the surface of the aggregates. However, as the effects are in the order of 10^{-4} , the authors do not believe that these effects are significant for the measurement results.

Based on these calculations, several phenomena were confirmed. First, the relationship between the penetration depth and the square root of the exposure time followed

Fig. 10 Calculated results compared with the experimental results at 20°C and 60°C.

Fig. 11 Dynamic microstructural changes for a surface node at (a) 20°C and (b) 60°C.

bilinear trends. The first slope was determined by the pore size distribution in the hardened cement paste under the pre-drying condition. The second slope was determined by the pore size distribution of the hardened cement paste after re-saturation. In the present finite differential calculations, the node that was exposed to the water reservoir controlled the rate of water supply through the mortar due to changes in the microstructure (see Fig. 11). The trends show that after the dynamic structural changes and increase in pore water volume, the system reached a quasi-steady state. Although the microstructures did not reach a stable state, a linear relationship is observed. In the present calculations, the balance of W_F and W_L with K_F and K_L resulted in a nearly constant slope after ten hours of water exposure at 20°C and ten hours at 60°C.

To predict the penetration depth in the target concrete, the second slope was determined experimentally over a period greater than two days. According to other studies, experiments should last more than one week for concrete (Taylor *et al.* 1999; Hall 2007). At higher temperatures, the second slope appears much earlier in the experiment.

The offset value for the second slope (y -intercept) was less than 10 mm. Using this offset value and the water contact time, the depth of water penetration in the concrete could be estimated. This value corresponds to the maximum depth of water penetration in the concrete.

Slope estimations for water penetration behaviors are challenging. Initially, the first slope was estimated using changes in the surface tension and the viscosity of the pore solution; however, after this calculation, it was found that the slope was affected by the balance between microstructural changes and the water transfer coefficients between fine pores and large pores. Under various temperature conditions, the C-S-H structures had different properties. Since the second slope showed trends that were contrary to those expected by pore solution surface tension and viscosity properties, it is challenging to explain the decreased slope without densification of the C-S-H structures. To predict water transport accurately, further quantitative data for microstructural changes coupled with sorptivity measurements are required.

5. Conclusions

As a step toward estimating the degree of concrete contamination following the Fukushima Daiichi accident, x-ray radiography was used to measure the sorptivity of mortar containing different cement and aggregate types under two different temperature conditions, i.e., 20 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. From the results, the following can be determined:

- 1) 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.
- 2) 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.
- 3) 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.

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