

Research Article

Effect of W/C Ratio on Durability and Porosity in Cement Mortar with Constant Cement Amount

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Water is often added to concrete placing for easy workability and finishability in construction site. The additional mixing water can help easy mixing and workability but causes increased porosity, which yields degradation of durability and structural performances. In this paper, cement mortar samples with 0.45 of W/C (water to cement) ratio are prepared for control case and durability performances are evaluated with additional water from 0.45 to 0.60 of W/C. Several durability tests including strength, chloride diffusion, air permeability, saturation, and moisture diffusion are performed, and they are analyzed with changed porosity. The changing ratios and patterns of durability performance are evaluated considering pore size distribution, total porosity, and additional water content.

1. Introduction

Concrete as a porous material has air/water permeable properties and this has a great influence on not only strength but also durability characteristics. Usually deteriorating agents which can cause steel corrosion like chloride ions and carbon dioxide intrude into concrete through pores or their connectivity [1–3]. Many techniques and models on durability have been proposed based on porosity for explaining permeation and diffusion mechanism [1–4]. In early-aged concrete, hydrates containing C-S-H and $\text{Ca}(\text{OH})_2$ are generated through chemical reaction with cement particles and water, and porosity with various pore distribution which are generated in the process can be the main route of water and gas. Many researches have been performed on the effects of curing condition, type of mix proportions, and mineral admixtures on the related porosity [5–8]; however, they have shown a qualitative evaluation for porosity without reliable explanation for the relationship between porosity and durability performance.

The strength and the related porosity have been studied for a long time [6, 9–11]. For deterioration analysis considering porosity changes, many researches have been carried out for chloride diffusion mechanism [1, 12, 13] and carbonation behavior [2, 4, 14, 15]. Porosity changes and its relationship with air/water permeability are also investigated [16–19].

These researches are for the normal concrete with suitable w/c ratio and air content. However, in construction site, water is often added for easy concrete placing and concrete passing between steel spacing. The added water can help easy workability and finishability but concrete with added water shows segregation of aggregates and degradation of performance both in strength and durability. In the concrete with the same unit cement content, hydration can be more activated with larger unit water content. But the consumed water for hydration reaction in cement paste develops to more pores which lead to reduction of strength and resistance to deterioration even in the same hydrate product amount. Porosity plays an important role in mass transport and is also considered as durability index [20]. In spite of the concrete

TABLE 1: Mix proportions.

w/c	Cement (kg/m ³)	Water (kg/m ³)	Sand (kg/m ³)	Air content (%)	Flow (mm)
0.45	340	153	1800	5.2	280
0.50	340	170	1800	3.5	330
0.55	340	187	1800	1.8	335
0.60	340	204	1800	0.1	360

TABLE 2: Physical properties of cement and sand.

Physical properties of aggregate	
Specific gravity (g/cm ³)	2.62
F.M	2.64
Physical properties of cement	
Specific gravity (g/cm ³)	3.15
Blaine (cm ² /g)	3,120
Chemical composition of cement (%)	
SiO ₂	21.5
Al ₂ O ₃	5.10
Fe ₂ O ₃	3.04
CaO	61.3
MgO	2.85
SO ₃	2.21
LOI	1.93

TABLE 3: Measuring conditions for MIP test.

Contacting angle	130°
Mercury surface tension	485 dynes/cm
Maximum head pressure	4.45 psi
Stem volume	0.392 mL
Bulb volume	5 cc
Pemetrometer constant	10.79/pF
High pressure measurement	33,000 psi

TABLE 4: Conditions for chloride diffusion test (NT BUILD 492).

Catholyte	10% NaCl
Anolyte	0.3 N NaOH
Temperature	20~25°C
Applied potential	30 V
Initial current	40~60 mA
Duration time	24 hours

samples with the same porosities, they may have different chloride diffusion coefficients due to the enhanced binding capacity in concrete with mineral admixture [17, 21]. For carbonation, the porosity is altered with carbonation process due to the formation of CaCO₃ [14, 15, 22, 23]. However, durability characteristics can be quantitatively evaluated and related to porosity in OPC (Ordinary Portland Cement) concrete controlled with the same curing and environmental conditions. In this paper, porosity is experimentally evaluated through MIP (Mercury Intrusion Porosimetry) for cement mortar with increasing additional water. Durability tests are

performed for the OPC mortar samples with the same age (91 days). Various durability tests including strength, chloride diffusion, air/water permeability, saturation, and moisture diffusion are performed. This paper presents how much durability performance and porosity change through adding water to normal concrete mix and shows the quantitative relationships between changes in porosity and durability performances.

2. Experiment Program

2.1. Mix Proportions and Curing Conditions. Cement mortar with OPC was prepared for MIP samples not to be interfered by coarse aggregate. For control case, cement mortar samples with 0.45 of W/C and 5.2% of air content are prepared. In order to consider the additional water for easy concrete placing, the samples with higher W/C ratio, and constant cement content are prepared through adding mix water. Surface saturated condition of sand is prepared for this mixing and finally 4 different mix proportions are considered as W/C of 0.45, 0.50, 0.55, and 0.60. Mix proportions are listed in Table 1 where the unit content of cement is fixed. The properties of cement and sand are listed in Table 2.

In early aged state, porosity shows relatively rapid reduction due to hydration so that the mortar samples have been cured for 91 days in water-submerged condition with 20°C of temperature. Tests of MIP and durability performance were performed for the samples at the same age. With higher w/c ratios, abundant bleeding water is observed and little segregation of aggregation is found. However, the samples are mortar, not concrete, so that segregation seems to be not critical.

2.2. Tests for Durability Performance

2.2.1. Porosity and Compressive Strength. Pore structure is developed with hydration reaction and porosity generally decreases with age in curing condition [3, 24]. For an evaluation of porosity in cement-based material, several techniques such as nitrogen adsorption method [25], image analysis, and MIP are widely utilized. MIP test is conventionally performed for its convenience and reliable results for capillary pores [26, 27]. Cement mortar samples cured for 91 days are submerged in acetone after breaking into a small size for stopping hydration process. After drying them in oven in 105°C for 24 hours, MIP tests are performed threefold for each W/C case. For the compressive test, cylindrical samples (100 mm of diameter and 200 mm of height) were prepared and the test was carried out based on JIS A 1108 [28]. Table 3

TABLE 5: Results of sorptivity, surface concentration, and moisture diffusion coefficient.

W/C	Sorptivity (S: kg/m ³ h ^{0.5})	Thickness (L: cm)	Area (A: cm ²)	Constant (B: mm)	Surface concentration (C _o : kg/m ³)	Moisture diffusion coefficient (D _m : m ² /h) × 10 ⁻⁷
0.45	0.17	5	25	0.02	42.89	9.1
0.50	0.18	5	25	0.02	48.73	12.4
0.55	0.24	5	25	0.02	53.89	14.3
0.60	0.44	5	25	0.02	56.43	24.2

TABLE 6: Regression analysis for various ranges of porosity and W/C ratios.

Pore diameter range	Y = A(X - 1) + 1	
	A	R ²
~0.01 μm	4.3682	0.7246
0.01~0.1 μm	2.3352	0.9839
0.1~1 μm	0.3412	0.1506
0.1~10 μm	0.9321	0.9765
10 μm~	0.5489	0.2400

shows measuring conditions for MIP test. In order to obtain appropriate sample, it is taken from the top, middle, and bottom location in the cylindrical sample.

2.2.2. Chloride Diffusion Coefficient. For an evaluation of resistance to chloride attack, diffusion coefficient is essential for prediction of service life and quantitative understanding of chloride behavior [12, 17, 29]. Chloride diffusion coefficient is calculated based on the guideline of NT BUILD 492 [30]. The average from 3 samples per each w/c case is obtained for the mortar samples at the age of 91 days. The middle part of cylindrical sample for compression test is taken with depth of 50 mm. Table 4 presents the test conditions and diffusion coefficients are calculated through (1) and (2). Silver nitrate solution (0.1 N, AgNO₃) was used as indicator [31]:

$$D_{nssm} = \frac{RT}{zFE} \cdot \frac{x_d - \alpha\sqrt{x_d}}{t}, \quad (1)$$

$$E = \frac{U - 2}{L}, \quad \alpha = 2\sqrt{\frac{RTL}{zFE}} \cdot \operatorname{erf}^{-1} \left[1 - \frac{2C_d}{C_0} \right], \quad (2)$$

where D_{nssm} is diffusion coefficient in non-steady-state condition from RCPT (m²/sec), R is universal gas constant (8.314 J/mol K), T is absolute temperature (K), L is thickness of specimen (m), z is ionic valence (= 1.0), F is Faraday constant (= 96,500 J/V mol), U is applied potential (V), t is test duration time (sec), C_d is the chloride concentration at which the color changes when using a colorimetric method for measuring x_d based on the references [31, 32], C_0 is chloride concentration in the upstream solution (mol/L), α is an experimental constant through (2), and erf^{-1} is the inverse function of the error function.

2.2.3. Water Evaporation. Concrete with larger pores permits larger water absorption in saturated condition and larger evaporation of water in drying process accordingly. Free water in cement mortar exists only in pores so that porosity is closely related with evaporation of water amount [33]. For this test, cubic mortar samples (50 × 50 × 50 mm) are prepared and their weights at the age of 91 days are measured after 1-week submerged condition. For 10 days, the changes in weight of mortar samples exposed to room condition (20°C and R.H. 55%) were monitored. With higher w/c ratio, segregation of aggregate can occur but, in the weight change, total weight is measured for entire volume. The effect of segregation is considered in the entire volume. Saturation can be calculated through the following:

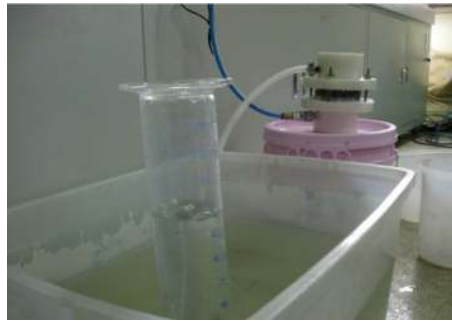
$$S(\%) = \frac{W_{\text{act}} - W_{\text{dried}}}{W_{\text{sat}} - W_{\text{dried}}} \times 100, \quad (3)$$

where W_{sat} , W_{act} , and W_{dried} are weights in saturated, room, and dried condition after 24 hours in 105°C in oven.

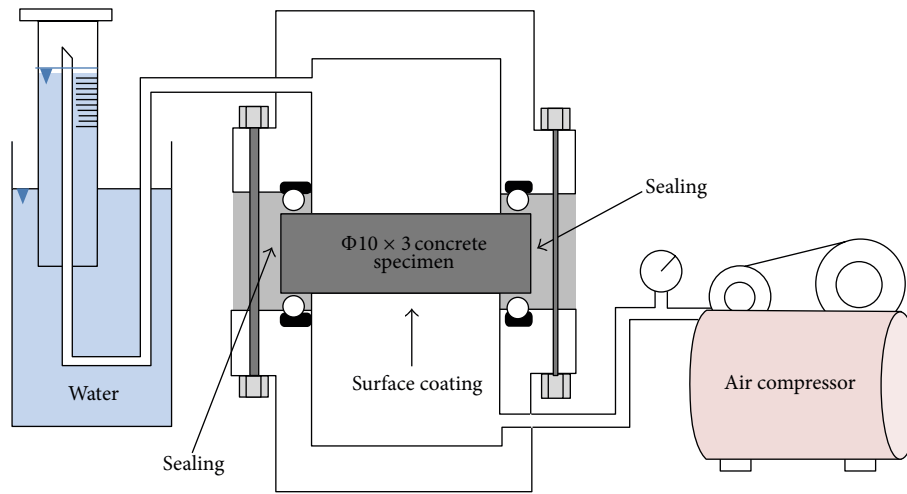
2.2.4. Air Permeability. So far, there have been no standards for air permeability test and various techniques are proposed based on Darcy's Law [34, 35]. For this study, mortar disk samples with 30 mm depth are fixed in the cylinder with 70 mm of diameter and subjected to air pressure of 0.2 MPa from bottom of the sample to upward. The air volume through the disk sample was monitored with time. This test is performed for samples at the age of 91 days and air permeability can be calculated through (4). As in Section 2.2.3,

TABLE 7: Results of regression analysis for normalized porosity and durability performance.

$Y = A(X - 1) + 1$	A	R^2
Y : w/c (water content)	0.6927	0.9755
Y : compressive strength	-0.4642	0.9678
Y : chloride diffusion coefficient	1.1446	0.9911
Y : saturation	0.0621	0.1625
$Y = B\sqrt{(X - 1)} + 1$	B	R^2
Y : water loss	0.5419	0.9984
Y : air permeability	1.4559	0.9809
$Y = C(X - 1)^2 + 1$	C	R^2
Y : sorptivity	6.1042	0.9809
Y : moisture diffusion coefficient	6.6166	0.9545



(a) Photos for test



(b) Schematic diagram for test

FIGURE 1: Test for air permeability.

entire volume including segregation is considered in the test of air permeability:

$$K = \frac{2P_2 h \gamma}{P_1^2 - P_2^2} \times \frac{Q}{A}, \quad (4)$$

where K is air permeability (cm/s), P_1 and P_2 are applied air pressure (0.2 MPa) and atmospheric pressure (0.1013 MPa), h is depth of disk sample (30 mm), A is area under air pressure

(0 m²), and γ is unit weight of air (1.205×10^{-6} kg/cm³). The test setup and its photo are presented in Figure 1.

2.2.5. Moisture Diffusion. Moisture diffusion is a major parameter since water is largely responsible for durability problems; however, experimental evaluation needs special control because of locally varying moisture and complex pore connectivity [36]. Recently, simple equation for moisture

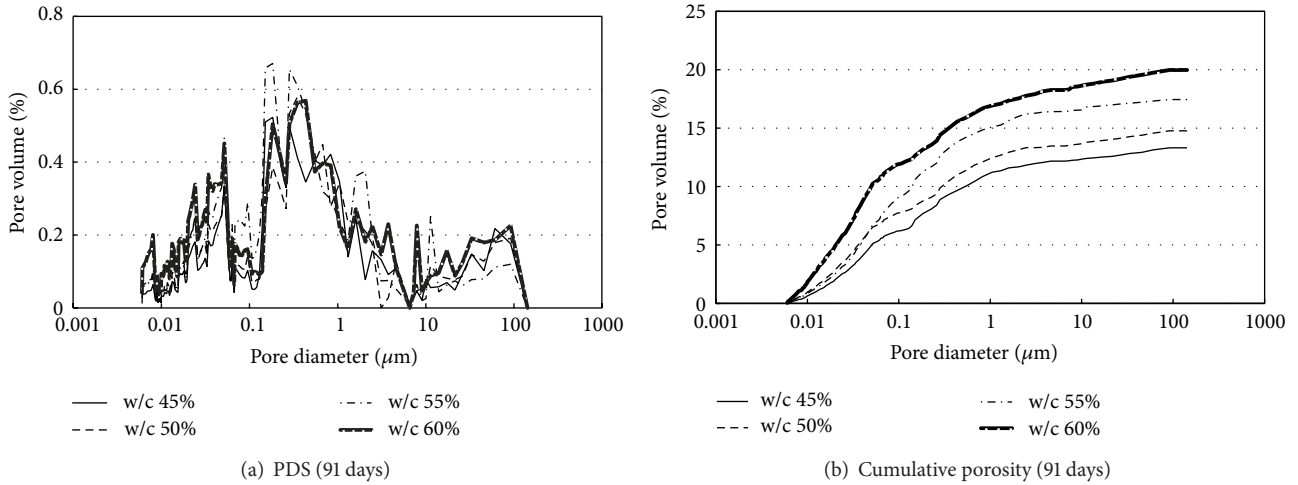


FIGURE 2: PSD and total porosity.

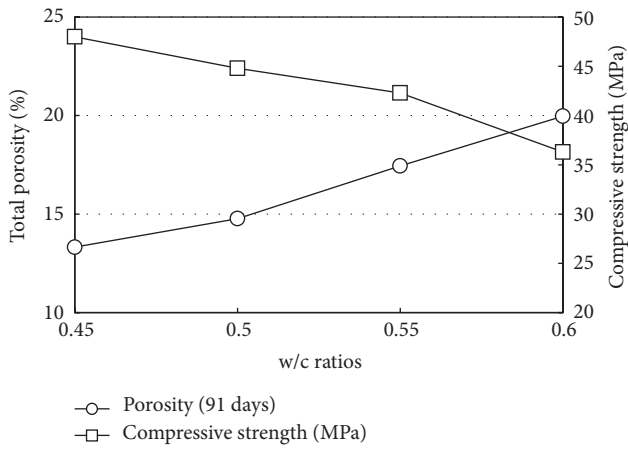


FIGURE 3: Strength and porosity with different W/C ratios.

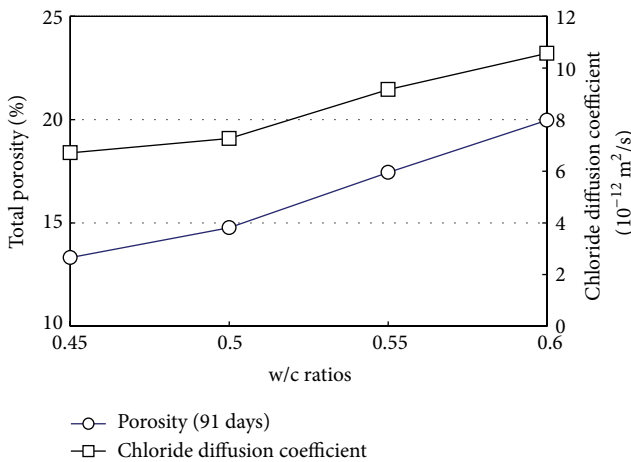


FIGURE 4: Chloride diffusion coefficient and porosity with different W/C ratios.

diffusion is proposed considering mass of diffusion and sorption like the following [36]:

$$\left(\frac{M}{A}\right)_t = B \left[1 - \exp\left(\frac{-St^{0.5}}{B}\right) \right] + C_0 L \times \left\{ 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[\frac{-D_m(2n+1)^2 \pi^2 t}{4L^2}\right] \right\}, \quad (5)$$

where M is mass of water from sorption and diffusion (kg), A is surface area (mm²), B is constant related to the distance from the absorbing surface (mm), S is sorptivity (kg/m²h^{0.5}), C_0 is surface moisture content (kg/m³), and L is length of specimen (mm). In this study, sorptivity for mortar sample (91 days) is obtained based on KS F 2609 [37] and moisture diffusion coefficient was calculated based on the results. Cubic samples (50 × 50 × 50 mm) are prepared and their sides were coated with epoxy resin for one-dimensional intrusion of water. As previously described, total volume of segregation is considered for the test.

3. Results of Durability Test and Porosity

3.1. Durability Test Results

3.1.1. *Compressive Strength and Porosity.* The larger water content in cement mortar leads coarse pore distribution. The results at the age of 91 days show typical increase in strength and decrease in total porosity with higher w/c ratio (larger additional water). Pore size distribution (PSD) and porosity are presented in Figure 2. Figure 3 shows changes in strength and porosity with w/c ratios. Averages from 3 samples are plotted for the evaluation of porosity and strength, respectively.

With increasing w/c ratio (additional water amount) from 0.45 to 0.60, porosity goes up to 150% and compressive strength is reduced to 75.6%. Although they have the same

cement amount, 33% additional water causes considerable changes in the performances.

3.1.2. Chloride Diffusion Coefficient and Porosity. Chloride diffusion coefficient is dependent on pore structure since pore can be both room for holding chloride ion and route for ion diffusion [29, 38]. In this test, the average from 3 samples shows clear increase in chloride diffusion coefficient with higher W/C ratio, which is presented in Figure 4 with measured porosity.

With higher W/C ratio, chloride diffusion coefficient linearly increases to 157%.

3.1.3. Water Evaporation and Porosity. For water loss, distinct difference is not observed within a few hours but can be observed with extended drying periods to 10 days. The samples with higher porosity can have larger room for keeping water so that water loss from each sample shows different amount with drying process. This shows consistent result with previous research [24]. In the saturation from (3), clear difference is not measured since the mortar with larger water loss has larger amount of free water as well. The water loss and saturation are presented in Figure 5 and they are plotted with measured porosity in Figure 6.

The amount of water loss increases to 7.65 g (w/c 0.45), 9.01 g (w/c 0.50), 9.88 g (w/c 0.55), and 10.57 g (w/c 0.60) after 10 drying days, which shows consistent behavior with porosity measurement.

3.1.4. Air Permeability and Porosity. The coarse pores in mortar with higher w/c ratio cause rapid air permeation and the results of air permeability with measured porosity are shown in Figure 7.

Air permeability increases to 192% when w/c changes from 0.45 to 0.60 and it shows relatively little increment over 0.50 of w/c.

3.1.5. Moisture Diffusion Coefficient and Porosity. Concrete with large product of hydrate has dense pore structure. Moisture diffusion coefficient is measured to increase with higher W/C ratio since it has higher sorptivity due to higher porosity. The results of sorptivity, surface concentration, and moisture diffusion coefficient are listed in Table 5 and presented in Figure 8 with measured porosity.

With increasing w/c ratio to 0.60, surface moisture content linearly increases to 132%. Sorptivity and moisture diffusion coefficient are shown to quadratic increase to 259% and 266%, respectively.

3.2. Porosity and Durability Performance

3.2.1. Analysis of Changes in Pore Size Distribution. In Figure 2, total porosity and PSD are measured. In order to analyze the changes in pore size, pore volumes in 5 groups of pore diameter are evaluated. Capillary pores which are closely related to mass transport are reported be within the size of $10^{-8} \sim 10^{-4}$ m [39] and the results from MIP range can cover

this range. Figure 9 shows the pore volume in 5 specified groups.

In each 5 divided region, measured porosities are averaged as one value and they are compared with W/C ratios. By doing so, the changes in porosity with different W/C ratios can be easily evaluated. Figure 10(a) shows the changes in porosity averages with different w/c ratios and Figure 10(b) shows their comparisons of normalized results by the case of W/C 0.45.

As shown in Figure 10, averaged porosities in 5 different range of pore diameter show interesting changes with increasing W/C ratio. In 2 groups of pore radius (below $0.01 \mu\text{m}$ and $0.01 \sim 0.1 \mu\text{m}$), relatively higher increasing ratio is measured with higher W/C ratios. The finer pores are easily filled with swelling of cement particles so that higher gradients of changing porosity are evaluated in the first 2 groups. The results of regression analysis shown in Figure 10(b) are listed in Table 6 with determinant coefficients. The gradient of normalized pore change in the first group ($\sim 0.01 \mu\text{m}$) is 4.3682 with 0.7246 of determinant coefficient. The second group ($0.01 \sim 0.1 \mu\text{m}$) has 2.3352 with 0.9839 of determinant coefficient.

3.2.2. Relationship between Porosity and Durability Performance. Analysis on durability characteristics with porosity is performed since relationships with w/c ratios may be practical but have no consideration of physical properties. Total porosity measure through MIP is normalized by the case of W/C 0.45 and compared with normalized durability test results. The results are shown in Figure 11 and those from regression analysis are listed in Table 7.

From the various tests, durability performances with linear relationship with porosity are evaluated to be W/C ratio (water content), compressive strength, and chloride diffusion coefficient. Nonlinear relationships of square root of porosity are found in water loss and air permeability. Sorptivity and moisture diffusion coefficient are related to square of porosity. Except for saturation, durability performances can be related to porosity change with high determinant coefficient.

This paper presents quantitative patterns and relationships between porosity and durability performances in the cement mortar with constant cement contents. In construction site or unavoidable conditions, adding water in fixed mix condition for temporarily easy concrete placing is often conducted; however, it is found that durability performances in cement mortar with added water significantly decrease with increasing porosity.

4. Conclusions

For OPC mortar with constant cement content and additional water content, various durability tests are performed and their results are investigated with derivation of pattern and relationship with porosity. The conclusions on effect of W/C ratio on durability and porosity in cement mortar with constant cement amount are as follows.

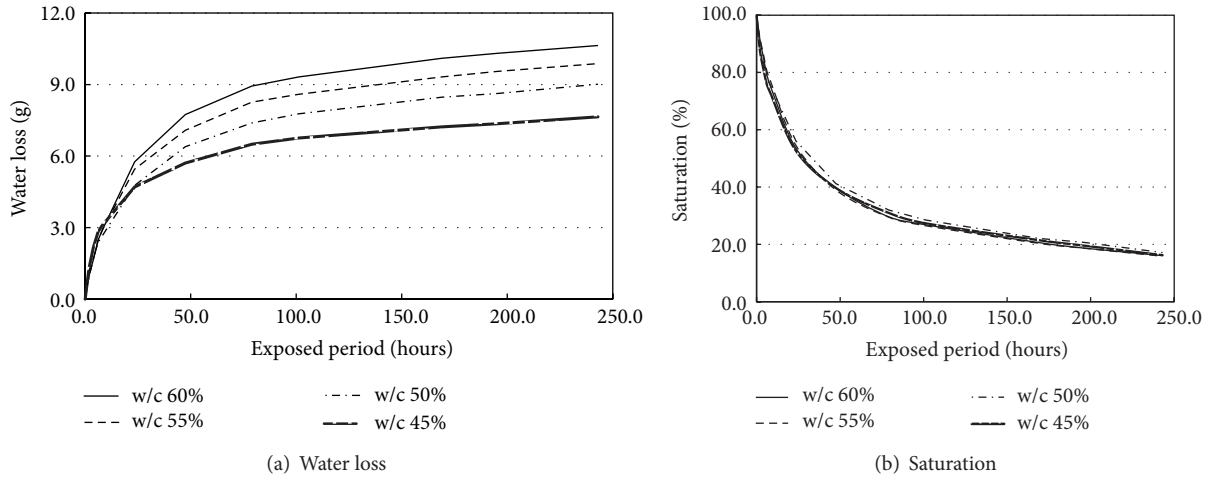


FIGURE 5: Water loss and saturation with W/C ratios.

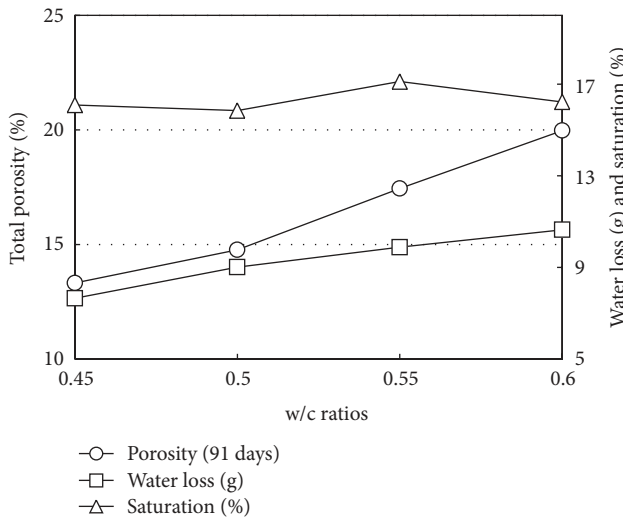


FIGURE 6: Water loss, saturation, and porosity with different W/C ratios.

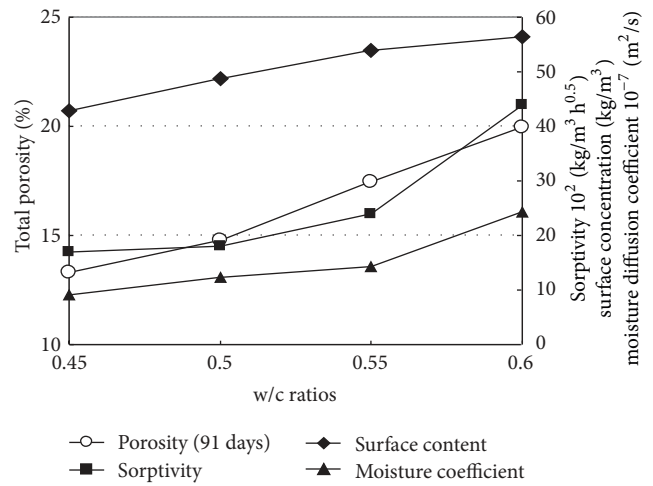


FIGURE 8: Sorptivity, surface concentration, moisture diffusion, and porosity with different W/C ratios.

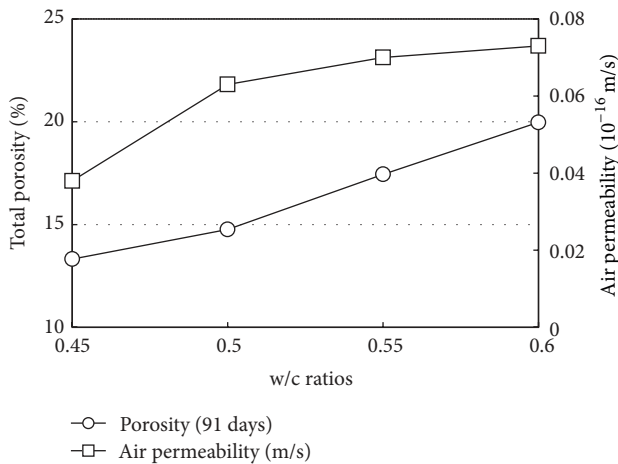


FIGURE 7: Air permeability and porosity with different W/C ratios.

(1) Cement mortar with constant W/C ratio of 0.45 and air amount 5.2% is prepared and its durability performances are quantitatively investigated with adding mixing water to 0.60 of W/C ratio. The increasing W/C ratio causes increasing porosity to 150% compared with control case (W/C 0.45). With increasing porosity, interesting patterns with porosity are evaluated, which are linear relationships (W/C ratio, compressive strength, and chloride diffusion coefficient), square root of porosity (water loss and air permeability), and square of porosity (sorptivity and moisture diffusion coefficient) with high determinant coefficient over 0.9.

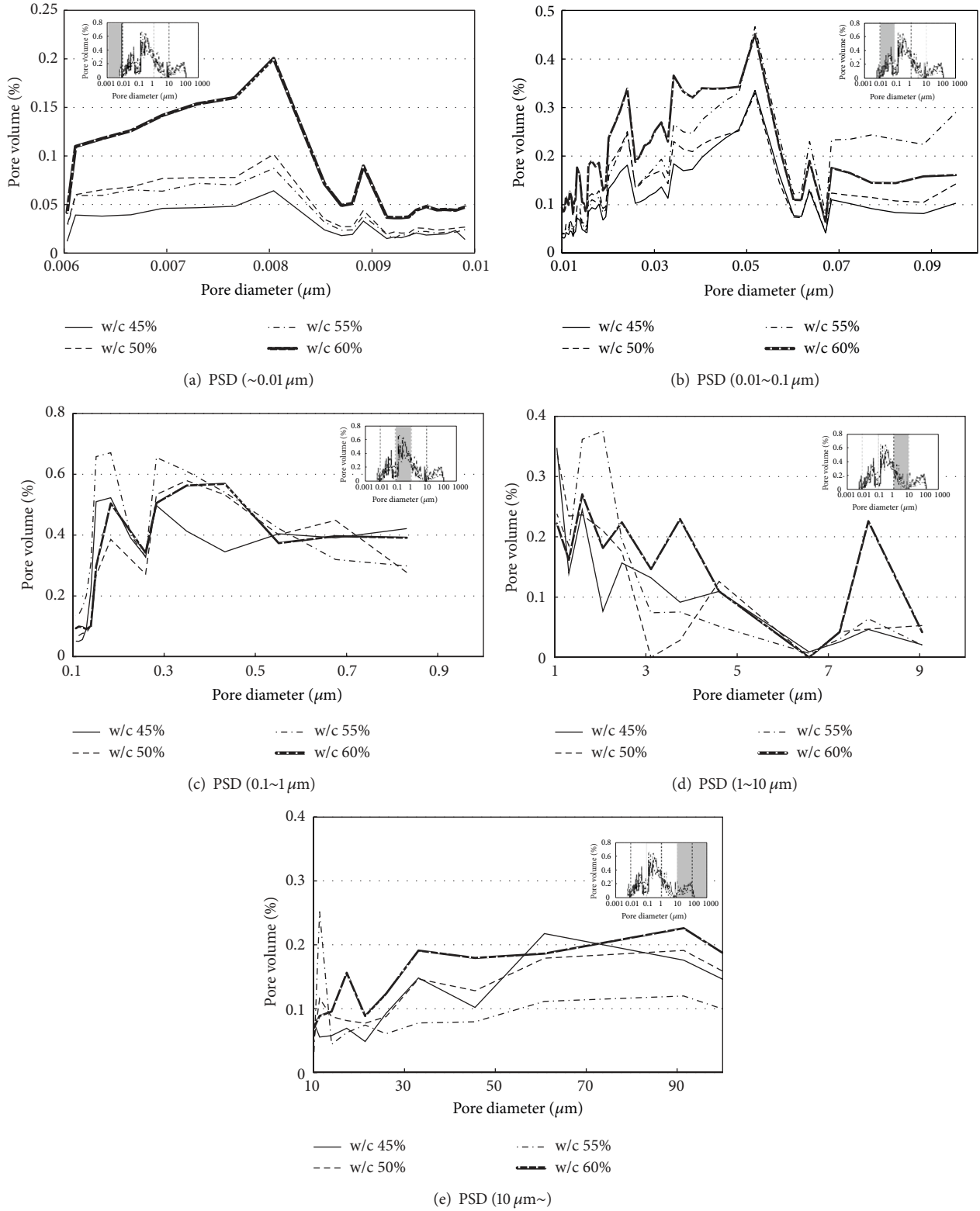


FIGURE 9: PSD in different pore radius.

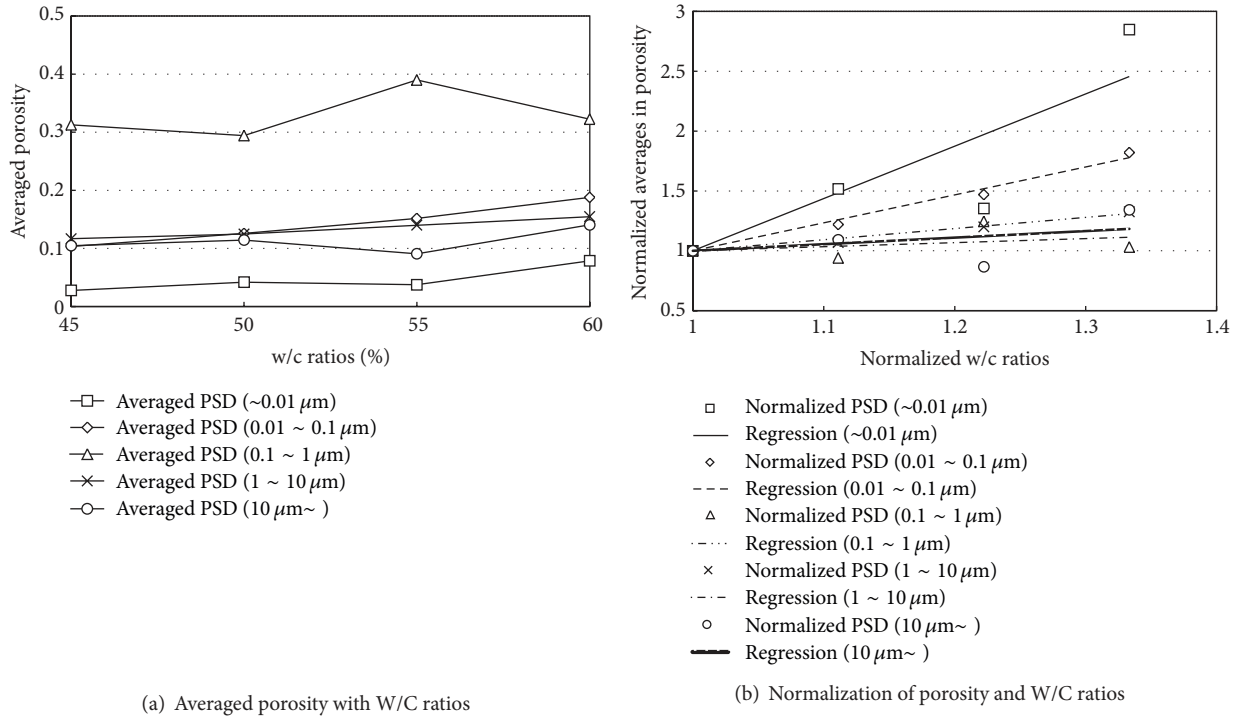


FIGURE 10: Changes in averaged and normalized porosity with W/C ratios.

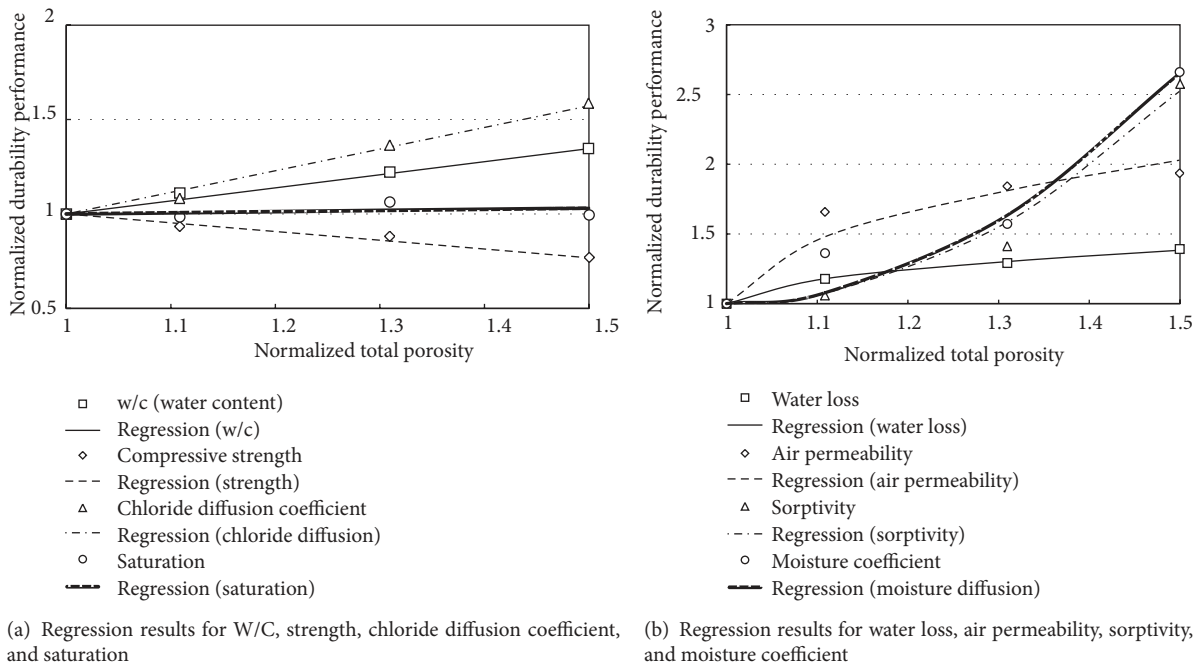


FIGURE 11: Relationships between normalized porosity and durability performance.

(2) With increasing water content from 0.45 to 0.60 of w/c (133% increase), it is evaluated that the increase ratios are 139% in water loss, 150% in porosity, 157% in chloride diffusion coefficient, 192% in air permeability, 259% in moisture sorptivity, and 266%

in moisture diffusion coefficient. In the compressive strength, it decreases to 75.6% for control case (W/C 0.45). This paper quantitatively presents how much and with what pattern the durability performances are changed with increasing mix water in cement mortar.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

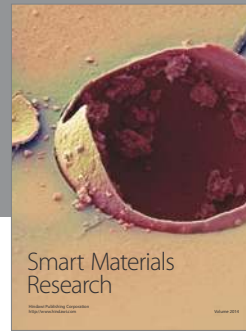
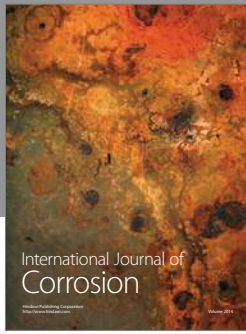
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