

Mechanical Properties of Calcium Leached Concrete

*Yoon-Suk Choi¹⁾ Young-Geun Kim²⁾ So-Yeong Choi³⁾ Eun-Ik Yang⁴⁾

^{1),2)} *Convergence Technology Division, Korea Conformity Laboratories, Seoul 153-803, Korea*

^{3),4)} *Dept. of Civil Engineering, Gangneung-Wonju National University, Gangneung 210-702, Korea*

¹⁾ yoons0305@kaist.ac.kr

ABSTRACT

Under ordinary processing and environmental conditions, properly designed concrete is a very durable material that can be expected to have a long service life. In radioactive waste repositories constructed underground, however, reinforced concrete member can remain in contact with groundwater for a long period. Thus, ground water in the form of pure water creates concentration gradients which lead to diffusion of calcium ions from the pore water and the degradation of underground concrete. Consequently, the mechanical property of concrete is potentially influenced by the leaching progress. Also, this phenomenon of concrete leaching is currently considered to be the key to long-term safety of nuclear structures.

Therefore, purposes of this study are to investigate not only the property changes of calcium leached concrete but also, the structural behavior of the concrete members associated with leaching attack. The test results clearly showed that the calcium leaching degradation is an increase in the material porosity and a global decrease in the mechanical performance.

1. INTRODUCTION

Radioactive waste repositories are typically constructed deep underground and on the shorelines of many countries. Also, these facilities require concrete with good long-term durability, as the concrete members will likely be in contact with groundwater for a long period. However, ground water in the form of pure water creates concentration gradients which lead to the diffusion of Ca ions from the pore water and the subsequent

¹⁾ Researcher

²⁾ Division Director

³⁾ Graduate Student

⁴⁾ Professor

degradation of underground concrete. Therefore, the main degradation factors are the gradual leaching of cement hydrate in pore water and chloride attack by sea water. This causes the concrete's porosity to increase and its strength to decrease. In addition, the chloride resistance will decrease due to the change of the pore structure. Thus, this phenomenon of concrete calcium leaching is currently considered to be the key to the long-term safety of nuclear structures.

Due to the long-term nature of this process of at least a few centuries, it is difficult to simulate it experimentally. Nevertheless, many studies have investigated the leaching of cement constituents from cement hydrate. However, most of these studies have been focused on the changes of intrinsic properties of concrete due to the leaching degradation. Also, the relationship between leaching degradation and the mechanical properties has not been well established. Therefore, the main objective of this study, which is based on calcium leaching phenomena, is to evaluate changes in the pore-structure associated with the dissolution of cement hydrate in concrete specimen. Also, this study will investigate the resistance against chloride penetration of calcium leached concrete and the effects of calcium leaching on the mechanical behavior of concrete specimen.

2. Experiments

2.1 Concrete mixture proportion

Table 1 shows the mix proportions of the concrete specimens with water to binder ratio of 0.4 and 0.5. In this experiment, Ordinary Portland Cement (American Society for Testing and Materials Type I) was used in all of the mixtures. In addition, to investigate the effect of mineral admixtures on leaching damage, some parts of the cement were replaced by mineral admixtures at a water/binder ratio of 0.5. The replacement ratios were 30 percent for blast-furnace slag (BFS) and percent for fly Ash (FA).

Table 1 Mix proportion of concrete

W/B (%)	S/a (%)	Unit weight(kg/m ³)					
		W	C	S	G	FA	BFS
40	43	170	425	721	934	-	-
50	45	173	345	782	933	-	-
	45	173	311	776	927	35	-
	45	173	242	778	929	-	104

2.2 Leaching acceleration method

In this test, instead of slow leaching kinetics obtained by means of de-ionized water or an electrochemical method, an ammonium nitrate solution was used to degrade the concrete specimens. The ammonium nitrate (NH₄NO₃) reacts initially with the calcium hydroxide (Ca(OH)₂) in the cement hydrates, leading to the appearance of a very soluble calcium nitrate (Ca(NO₃)₂) and the emanation of gaseous ammoniac NH₃ (Carde 1996). Unfortunately, these phenomena do not occur under natural conditions.

Under natural conditions, there is a chemical equivalence between the $\text{Ca}(\text{OH})_2$, C S H, and each ion component in the pore solution from the viewpoint of phase equilibrium. If the Ca^{2+} concentration in the pore water decreases, the $\text{Ca}(\text{OH})_2$ dissolves, thus supplying additional $\text{Ca}(\text{OH})_2$ ions from the cement hydrates to maintain the chemical equivalence. After the portlandite is completely dissolved, the Ca^{2+} ions supplemented from C-S-H start to dissolve and C-S-H finally degrades to SiO_2 gel. Nevertheless, these differences between the artificial condition and the natural condition do not change the mechanism of calcium leaching from the concrete.

2.3 Test method for porestructure

A mercury intrusion porosimetry (MIP) test based on ASTM D4284 was conducted to measure the pore size distribution of calcium leached concrete. As shown in Fig. 1, a six mole concentration of an ammonium nitrate solution was used and the concrete specimens were totally immersed for a predetermined period (15, 30, 60, 90, 180 and 365 days). After a specified period, the specimens were cut and shaped into cubes of $10 \times 10 \times 10$ mm in size using a diamond cutter for mercury intrusion porosimetry (MIP) method. After being vacuum-dried samples, the micro-pore size distribution (5 nm to $10 \mu\text{m}$), bulk density, and porosity were measured by MIP test.

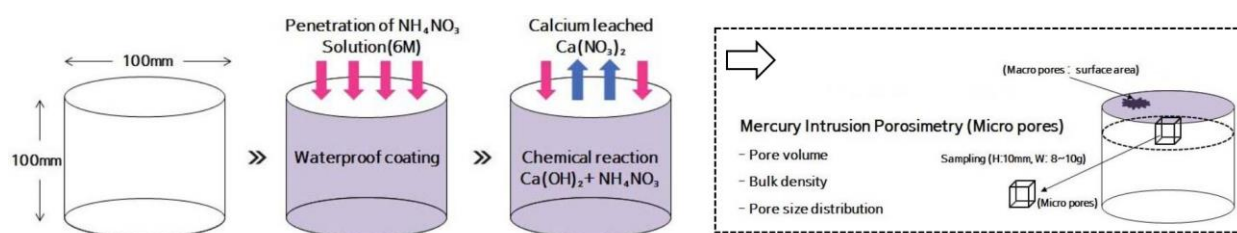


Fig. 1 Scheme of the porestructure test method

2.4 Test method for chloride penetration resistance

A rapid chloride permeability test (RCPT) was performed after the chemical acceleration leaching test. In this test, a water-saturated, 50 mm thickness, 100 mm diameter concrete specimen was subjected to 30V of applied DC voltage for eight hours using the apparatus shown in Fig. 2. In one reservoir was a 3.0 percent NaCl solution, and in the other reservoir was a 0.3 M NaOH solution. After RCPT test, the concrete specimens are removed and split, and the thickness of the chloride penetration is determined in one half of the specimen using a colorimetric technique in which a silver nitrate solution is used as a colorimetric indicator.

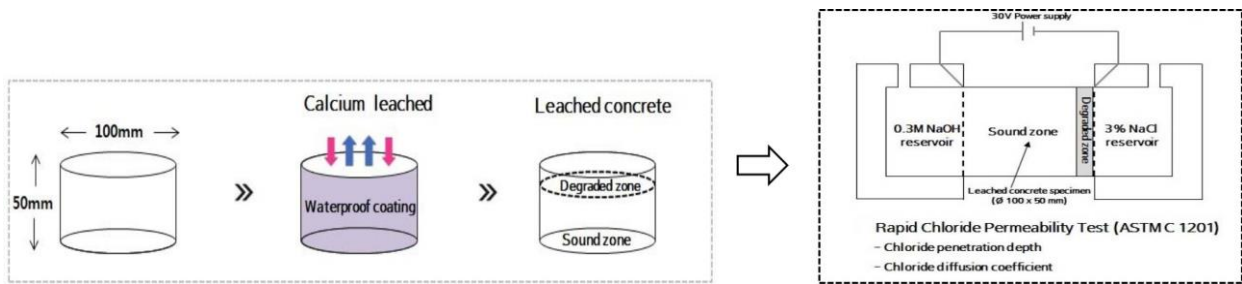


Fig. 2 Scheme of the RCPT method

2.5 Test method for compressive behavior

For the compressive strength of calcium leached concrete specimens, a cylinder (100 mm diameter, 200 mm height) was prepared based on ASTM C 39. The compressive strength tests for the reference and leached specimens were conducted with leaching periods 30, 60, 90, 180, 365 and 730 days. Fig. 3 shows the scheme of the compression test on leached and sound concrete. Both sound and leached specimens were subjected to a compressive load to measure their compressive strengths. The displacement value was checked during the load. The force applied on the specimens was measured during the test. Also, the compressive load was supplied by a universal testing machine (UTM) with a capacity of 1000 kN. Each compressive strength value was the average of three specimens.

2.6 Test method for flexural strength

In order to simulate the effect of a leaching attack, RC members investigated in this study for flexural failure tests consisted of two pairs of concrete members sized 20 cm×30 cm×2.2 m. One of these is a sound RC member and the other is a leaching damaged RC member. As shown in Fig. 3, the chemical acceleration method was chosen for applying the leaching damage to RC member. The specimen section, reinforcement details, and loading points of specimens used in the experiment are also shown in Fig. 3.

A four-point controlled loading method was applied in this study. When the central displacement at the center of the member reached $0.5\Delta_y$, Δ_y , and $2\Delta_y$, the vertical load was reversed and applied monotonically, where Δ_y is the yielding displacement of the member obtained from a load-displacement curve. The vertical loads were applied using hydraulic jacks with a capacity of 300 kN. To obtain the vertical displacement with an increasing load, a linear variable displacement transducer (LVDT) was installed vertically on the bottom of the center section.

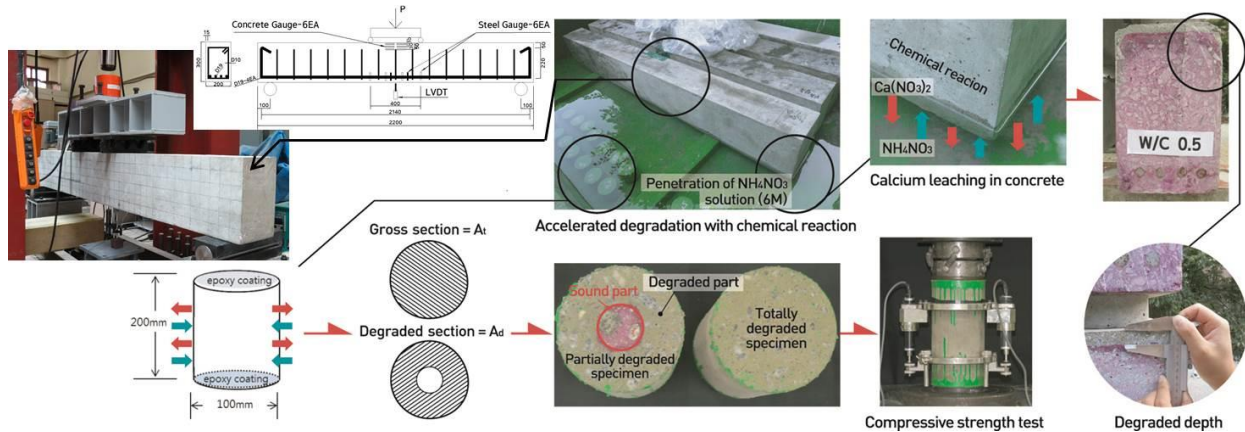


Fig. 3 Test method for the mechanical behavior of calcium leached concrete

3. Results and discussion

3.1 Porestructure of calcium leached concrete

Fig.4 and Fig.5 shows the change in the pore size distribution between the sound and leached concrete at a depth of 10 mm for during 365 days. In Fig. 4, the pore size of the sound concrete mainly ranges from 30 nm to 100 nm and shows a nearly constant trend regardless of the curing duration. This tendency appears in the W/B 0.4, W/B 0.5 and with FA replacement. In the case of BFS replacement, however, a different distribution was evident. That is, the pores, from 30 nm to 100 nm, were nearly filled with BFS particles or pozzolan reaction substance, so the peak of the pore size disappeared.

Meanwhile, Fig. 5 shows that as the leaching period became longer, the pore volume within 200 nm to 500 nm in diameter also greatly increased. Also, the volumes of pores larger than 200 nm rapidly increased during the initial leaching period while those below 50 nm gradually increased regardless of the water-binder ratio. That is, the leaching of calcium ions from calcium silicate hydrate (C-S-H) was not easy, unlike the leaching of portlandite ($\text{Ca}(\text{OH})_2$). In OPC, the primary hydrate phases are C-S-H gel and portlandite. According to another study (Haga, 2005) involving a mortar leaching test, the changes in the pore volume assumed that pores 50 nm or smaller were attributable mainly to the C-S-H gel, while pores larger than 200 nm were attributable mainly to portlandite.

It was also recognized that pore size distribution measurement by MIP presents some problems. For instance, it is reported that pore diameters obtained from MIP measurements are smaller than those observed with a scanning electron microscope (SEM). This is thought to depend on a factor known as the “bottleneck phenomenon.” However, portlandite in hardened cement is a large crystal and the C-S-H gel is a very small crystal in comparison. Therefore, it was believed that the change in pore size distribution caused by the dissolution of portlandite and C-S-H gel was distinguishable. It is recognized as being questionable as to whether it is appropriate to classify the pore volume using a pore diameter cut-off at 200 nm. In this study, however, it has been

confirmed that there is a good correlation between the dissolution of portlandite and the increase in the volume of pores larger than 200 nm in leaching tests of cement hydrate. From these results, it appears that much portlandite is removed by leaching and that the part of the C-S-H is also removed. Similar results were noted in the concrete specimen. Although the similar voids increased, it is considered that the effect due to calcium leaching is more serious in the concrete specimen due to the interfacial transition zone (ITZ) near the particles of coarse aggregate.

3.2 Porestructure of calcium leached concrete

As previously mentioned, Portland cement-based material is a porous construction material. The capillary porosity and connectivity of these capillary pores are the most important characteristics of pore system related to the diffusivity of concrete. Since, the critical pore diameter represents the grouping of the largest fraction of interconnected pores influencing the transport properties. Thus, this section tried to investigate to the chloride diffusion after the leaching degradation.

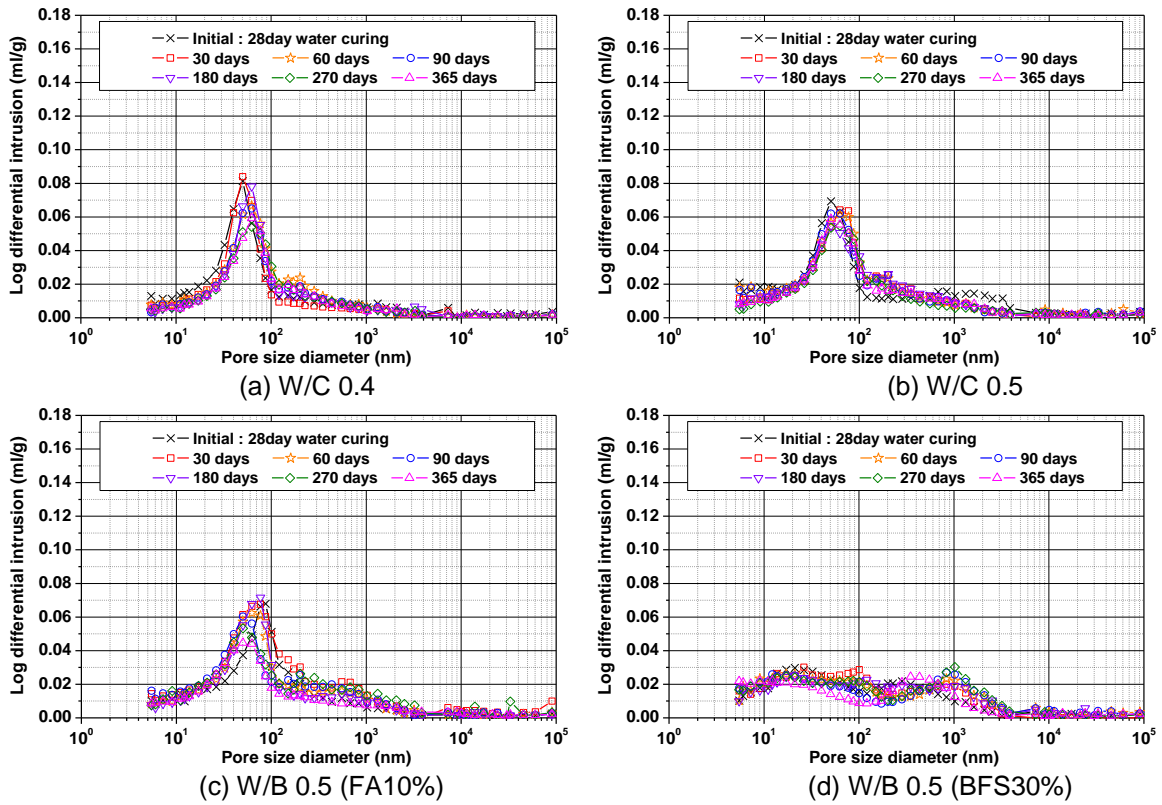


Fig. 4 Pore size distribution of the sound concrete specimen under water curing

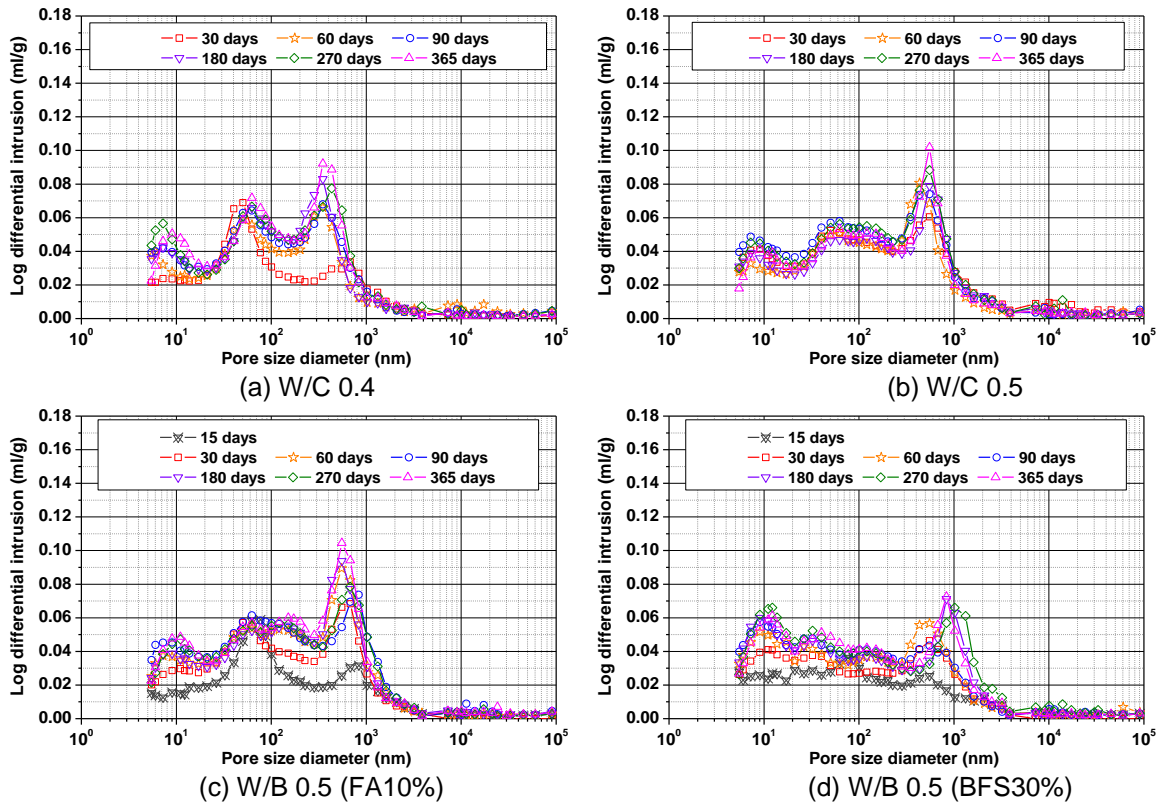


Fig. 5 Pore size distribution of the leached specimen for 365 days

Fig. 6 shows the result of the chloride diffusion coefficient as measured by the RCPT at each leaching period. According to the results, the chloride diffusion coefficient decreased clearly with an increase in the curing time and decreased at a lower-binder ratio. However, the diffusion coefficient of chloride after the leaching test greatly increased with the leaching period and the degradation depth. In the case of OPC, the diffusion coefficient increased by approximately 1.5 times to 2.5 times. Specifically, the diffusion coefficients of FA and BFS concrete showed increases of three times to six times.

Yang (2006) reported that the linear relationship between the critical pore diameter and steady-state diffusion coefficient as well as the critical pore diameter and non-steady-state diffusion coefficient are fairly good. He also indicates that the diffusion coefficients are linearly related to the capillary pore volume (pore diameter between 30 to 10,000 nm) and the critical pore diameter. In this study, therefore, the diffusion coefficient with leaching duration is increased because the leaching action makes the surface part of a concrete member more porous (especially for pores 200 nm in size), as shown in Section 3.2. Also, it is desirable to increase the cover depth of a concrete member exposed to leaching attack to improve its resistance of chloride penetration.

Generally, when admixtures such as FA and BFS are blended into concrete, the chloride diffusion is lower than of normal concrete. The use of FA or BFS increases the chloride binding capacity due to improved chemical and physical binding. However, as

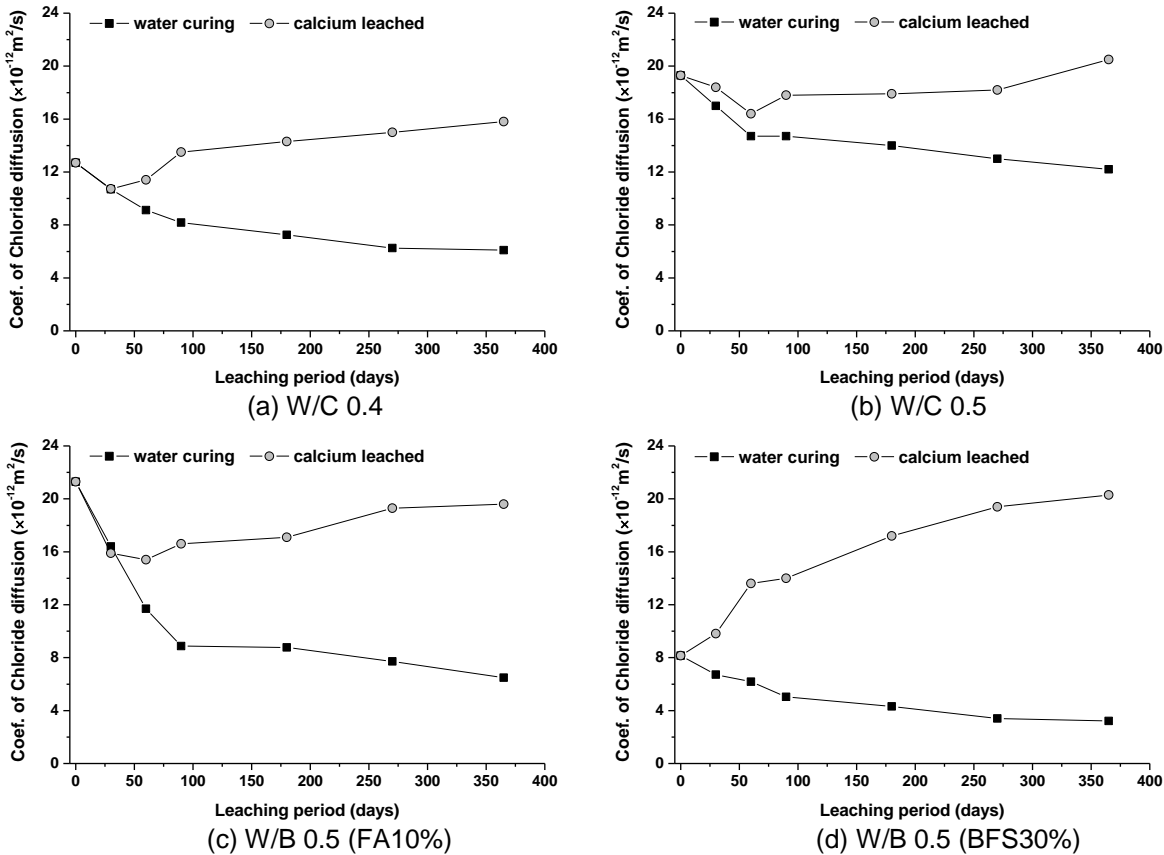


Fig. 6 Chloride diffusion coefficient of leached concrete using RCPT

generally known, the calcium hydroxide produced from hydration of Portland cement is partially consumed by the pozzolanic action of blast furnace slag and fly ash. Further, leaching phenomena leads to a dissolution of Ca ions from portlandite (Ca(OH)_2). Therefore, it is concluded that a lack of portlandite by leaching degradation in pozzolanic concrete leads to a faster chloride diffusivity. On the other hand, if the concrete has not had a sufficient curing period in regards to the reaction with portlandite, even when the mineral admixture is mixed with cement paste, the mineral admixture is not efficient against both leaching degradation and chloride attack.

3.3 Compressive strength of calcium leached concrete

Fig. 7 shows the compressive strength of sound concrete according to the water curing age and that of degraded concrete according to the leaching period. The ratio of the degraded zone (A_d) to the total area (A_t) is also shown in Fig. 7. According to Fig. 7, the compressive strength at 730 days for sound concrete showed a higher value than that at 28 days for all mixtures. In contrast, the compressive strength of the leached specimen gradually decreased with increase in the degraded ratio.

As shown in Fig. 7 (a), the compressive strength of leached concrete on the 730th day of the leaching period decreased to about 28 percent of the sound concrete (water curing condition). Also, according to Fig. 7 (b), a significant decrease (approximately 13 percent of sound concrete) of compressive strength in case of W/B 0.5 occurred on the 730th day of the leaching period and the leaching degraded ratio was 93 percent at this time. Therefore, these results clearly show that the leaching process leads to a decrease in the compressive strength.

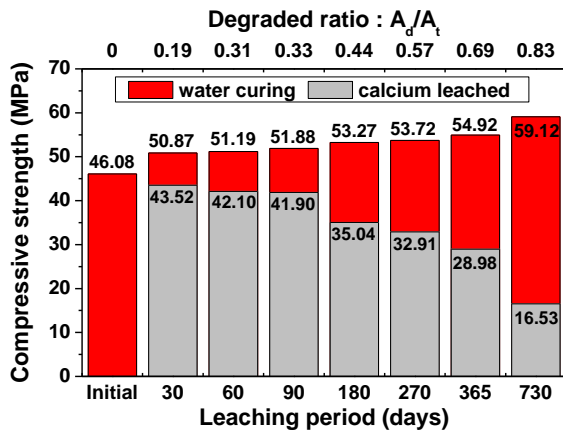
In general, capillary pores larger than 50 nm, referred to as macro-pores in modern literature, are more influential in determining the strength and impermeability characteristics, whereas pores smaller than 50 nm, referred to as micro-pores, play an important role in drying shrinkage and creep (Mehta, 1993). In this study, the volumes of pores larger than 200 nm increased due to hydrate leaching. That is, a loss of strength was caused mainly by a change in the pore size for pores larger than 200 nm.

Meanwhile, when the mineral admixture is blended into concrete, it is expected to increase the resistance against calcium leaching. However, the effect of the mineral admixture was minor in this study. Contrary to our expectations, the loss of strength in the concrete blend with the mineral admixture was larger than the non-replacement result. Thus, it appears that the leaching speed was faster than the pozzolanic reaction (leaching started at 28 days). Therefore, a sufficient curing duration must be allowed for concrete blended with a mineral admixture to prevent a loss of compressive strength due to leaching.

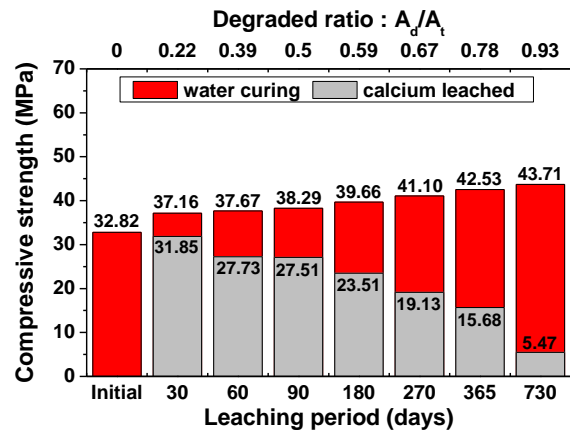
3.4 Flexural strength of calcium leached RC member

The displacements measured at each loading step by the LVDT installed at the mid-span of the members were compared. The displacement curves of the members are shown in Fig. 8 (a) through (c). Table 2 shows the initial cracking, yield load, peak load and collapse load for each specimen.

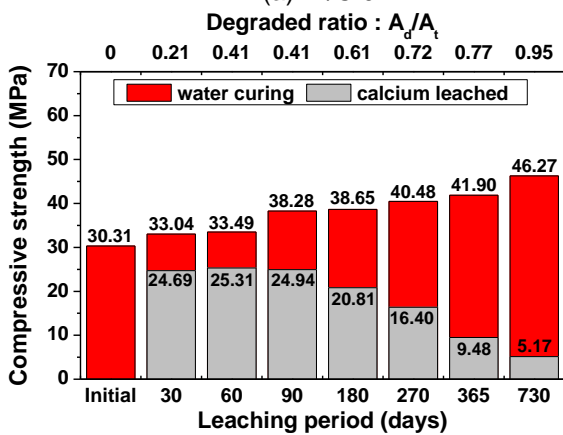
The first cracking load is the value of the load at the end of the initial linear zone in the load-displacement curve. The yield load is the load when the rebar yielded, which was detected by strain gages on the rebar. The peak load is the maximum load of the load-



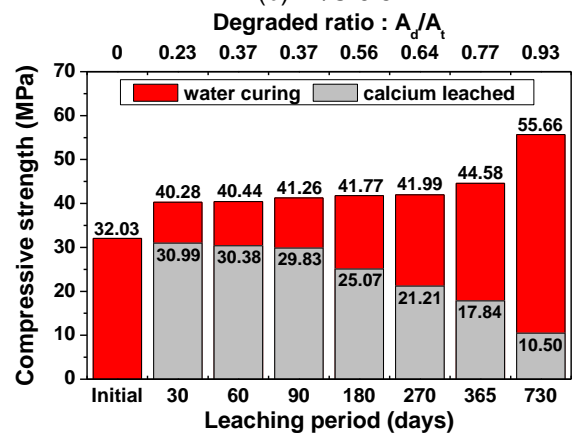
(a) W/C 0.4



(b) W/C 0.5



(c) W/B 0.5 (FA10%)



(d) W/B 0.5 (BFS30%)

Fig. 7 Compressive strength of calcium leached concrete

displacement curve. The load-displacement curve of all members until the initiation of cracks increased linearly and was proportional to the load. After the initial cracking, deflection increased nonlinearly until the maximum load was reached.

As shown in Fig. 8 and Table 2, the initial crack load (P_{cr}) of the damaged RC member is similar to that of sound concrete. Also, the maximum load (P_u) and the yielding loads (P_y) of the damaged member was slightly smaller than that of the sound member. However, the measured strain and P_y was significantly at P_u increased in the damaged RC member. Further, according to Fig. 8, after the maximum load is achieved, a drop in the slope is observed in the damaged member. Therefore, it appears that the post peak capacity of RC members decreased when the compressive zone was damaged by the leaching attack.

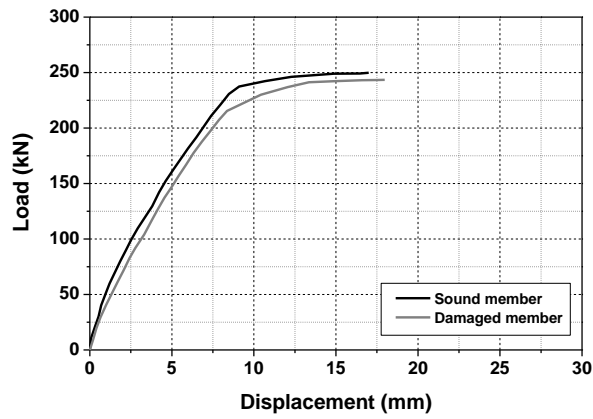
4. CONCLUSIONS

- 1) When the leaching period increases, the pore volume for pores 200 nm to 500 nm in diameter also increases. Further, the volumes of pores larger than 200 nm increase

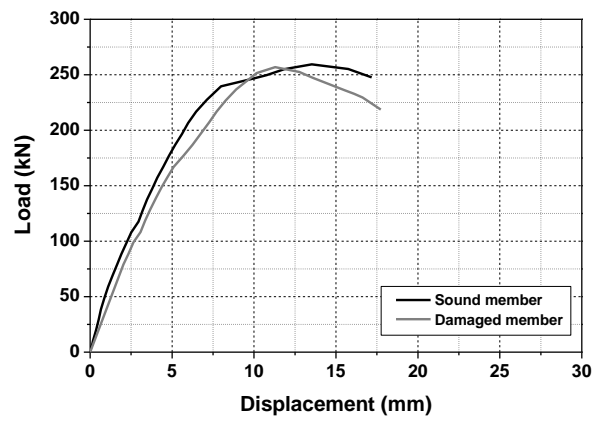
during the initial leaching period while those below 50 nm increase gradually regardless of the water-binder ratio.

Table 2 Experimental values

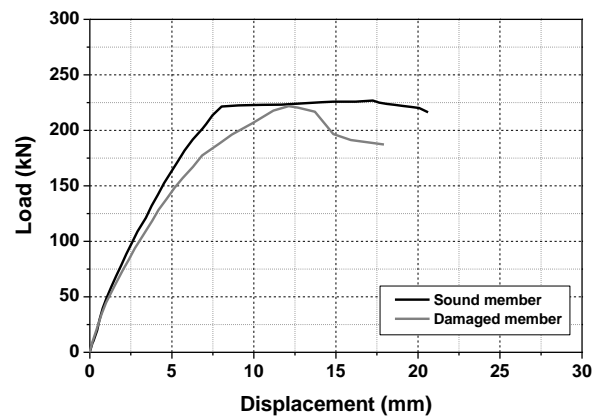
		OPC		FA		BFS	
		Sound	Damaged	Sound	Damaged	Sound	Damaged
Initial Cracking	P_{cr} (kN)	21	20	20	20	20	20
	Δ_{cr} (mm)	0.32	0.28	0.36	0.29	0.44	0.41
	M_{cr} (kN·m)	8	8	8	8	8	8
	\varnothing_{cr} (1/m)	0.0008	0.0008	0.0009	0.0006	0.0007	0.0008
	ε_{cr}	0.00012	0.00011	0.00011	0.0001	0.00011	0.00011
	Nutral axis (mm)	146	143	121	161	134	153
Yielding Point	P_y (kN)	246	215	240	237	223	206
	Δ_y (mm)	12.28	8.36	7.99	8.91	10.49	9.9
	M_y (kN·m)	98	86	96	95	89	83
	\varnothing_y (1/m)	0.0183	0.0176	0.0161	0.0157	0.0125	0.0164
	ε_y	0.0018	0.0022	0.0017	0.0020	0.0016	0.0017
	Nutral axis (mm)	104	126	108	121	103	126
Peak Point	P_u (kN)	250	243.5	259	256	227	222
	Δ_u (mm)	17	18	13.52	11.29	17.25	12.12
	M_u (kN·m)	100	97	104	103	91	89
	\varnothing_u (1/m)	0.0171	0.0250	0.0188	0.0250	0.0120	0.0168
	ε_u	0.0018	0.0030	0.0019	0.0027	0.0016	0.0018
	Nutral axis (mm)	108	127	106	119	111	124
Collapse Point	P_c (kN)	250	243.3	248	219	216	187
	Δ_c (mm)	17.5	18.1	17.18	17.73	20.62	17.93
	M_c (kN·m)	100	97	99	87	89	75
	\varnothing_c (1/m ⁻¹)	0.0169	0.0270	0.0181	0.0300	0.0126	0.0164
	ε_c	0.0018	0.0030	0.0020	0.0030	0.0016	0.0022
	Nutral axis (mm)	108	127	102	103	114	135



(a) OPC (W/B 0.5)



(b) W/B 0.5 (FA10%)



(c) W/B 0.5 (BFS30%)

Fig. 8 Load-displacement curve

2) In the case of the RCPT, the chloride diffusion coefficient of leached OPC increased by approximately 1.5 times to 2.5 times. Also, the coefficients of the leached concrete

blended with FA and BFS showed increases of three to six times, respectively. Meanwhile, use of the mineral admixture did not show useful results for both calcium leaching degradation and chloride attack. Therefore, a sufficient curing period must be allowed for concrete blended with a mineral admixture to resist leaching degradation.

- 3) The residual strength of the leached part with OPC was in the range of 26 percent to 46 percent. In the mineral admixture replacement case, upon blending with BFS, the residual strength of the degraded zone was in the range of 23 percent to 45 percent. Specifically, the residual strength of FA concrete was in the range of 20 percent to 28 percent. In case of the leaching degraded ratio which exceeds 90 percent, however, the residual strength was in the range of 6 percent to 13 percent.
- 4) The post peak capacity and the flexible rigidity of the leaching damaged RC member decreased due to the leaching degradation on the compressive zone. The curvatures of the leached member increased significantly compared to that of sound concrete. Thus, it appears that the possibility of sudden failure may increase as a result of leaching degradation.

ACKNOWLEDGMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2010-0023118).

REFERENCES

- Carde, C., Escadeillas, G., François, R., Torrenti, J.M. (1996), "Leaching of both calcium hydrate and C-S-H from paste: modeling the mechanical behavior," *Cem. Concr. Res.*, **26**(8), 1257–1268.
- Choi, Y.S., Yang, E.I. (2013), "Effect of Calcium Leaching on the Pore Structure, Strength, and Chloride Penetration Resistance in Concrete Specimens," *Nucl. Eng. Des.* **259**, 126–136.
- Haga, K. (2005), "Change in pore structure and composition of hardened cement paste during the process of dissolution," *Cem. Concr. Res.*, **35**(5), 943–950.
- Mehta, P.K. (2005), "Concrete: Microstructure, Properties, and Materials," 3rd Ed, McGraw-Hill.
- Yang, E.I., Choi, Y.S. (2011), "Characteristics of pore structures and compressive strength in calcium leached concrete specimens," *J. Korea Concr Inst.*, **23**(5) 647–656. [in Korean]
- Yang, C.C. (2006), "On the relationship between pore structure and chloride diffusivity from accelerated chloride migration test in cement-based materials," *Cem. Concr. Res.*, **36**(7), 1304–1311.