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Evaluation on Surface Scaling and Frost Resistance for Concrete Deteriorated due to Cyclic Freezing and Thawing with Inherent Chloride

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The purpose of this study is to evaluate freezing-thawing and surface scaling resistance in order to examine the frost durability of concrete in a chloride-inherent environment. The mixing design for this study is as follows: 3 water binder ratios of 0.37, 0.42, and 0.47; 2-ingredient type concrete (50% OPC concrete and 50% ground granulated blast-furnace slag), and 3-ingredient type concrete (50% OPC concrete, 15% fly ash, and 35% ground granulated blast-furnace slag). As found in this study, the decrease of durability was much more noticeable in combined deterioration through both salt damage and frost damage than in a single deterioration through either ofthese; when using blast-furnace slag in freezing-thawing seawater, the frost durability and surface deterioration resistance was evaluated as higher than when using OPC concrete. BF 50% concrete, especially, rather than BFS35%+FA15%, had a notable effect on resistance to chloride penetration and freezing/expansion. It has been confirmed that surface deterioration can be evaluated through a quantitative analysis of scaling, calculated from concrete's underwater weight and surface-dry weight as affected by the freezing-thawing of seawater.

Keywords : *salt damage, freezing-thawing, surface scaling, ground granulated blast-furnace slag, ternary concrete*

1. Introduction

In terms of environmental conditions, seawater-affected concrete is different from ordinary concrete in that it is subject to combined deterioration caused by salt penetration and diffusion, abrasion by water droplets, dry-wet repetition, and the freezing-thawing of seawater. These multiple deterioration factors combine to result in much shorter durability of marine concrete structures than through the ordinary speed of chloride diffusion. This is thought to be because the deterioration stress, e.g. seawater penetration and freezing-thawing, is increased to destroy the surface structure of concrete and bring about a synergy effect. There is, however, little research on durability evaluation that considers the combined deterioration by salt damage and freezing-thawing.[1),2)]

Alternatively, the surface deterioration of concrete is generally due to the expansion pressure occurring when the moisture inside and outside concrete is frozen. Since the expansion pressure caused by the freezing of seawater is higher than that caused by the freezing of ordinary water, the seawater freezing outside the concrete leads to a further sharp surface deterioration.[3)] That is, surface deterioration can be more rapid than the destruction of the internal structure of concrete by seawater, and a great decrease of soundness of coated concrete can speed up the progress of salt damage.

This study, therefore, aims to evaluate the decrease of durability and the scaling deterioration of concrete under the combined deterioration conditions created in a marine environment (e.g. chloride penetration and freezing-thawing), to assess the frost durability and surface scaling deterioration of concrete caused by the freezing of inherent chloride and seawater, and to examine the combined decrease of durability of concrete under the condition of combined deterioration by salt damage and frost damage.

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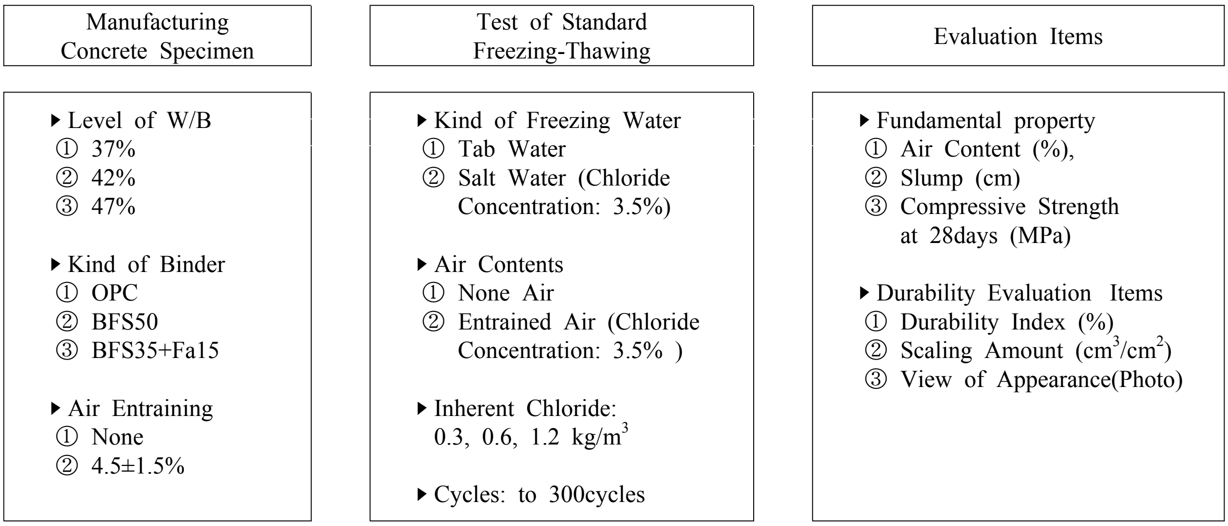


Fig. 1. Process and guide line of this study

2. Outline of experiment

2.1 Experimental plan

Fig. 1 shows a summary and the progress of this study; in order to evaluate the frost durability and scaling deterioration of concrete caused by freezing-thawing under a chloride-inherent environment, artificial seawater[4)] with chloride of 3.5% concentration was prepared as frozen water and tap water. In the assumption that chloride exists inside concrete, chloride contents of 0.3, 0.6, and 1.2 kg/m^3 were injected into the concrete.

The water binder ratio for concrete was set at 37, 42, and 47%. To evaluate the basic physical properties of concrete, two kinds of binders were composed of OPC (Ordinary Portland Cement), BFS (2-ingredient type), BFS + Fly Ash (3-ingredient type). Also, in order to evaluate relative dynamic modulus and surface scaling amount, freezing-thawing tests were performed according to the entrainment of air contents, the W/B ratio (water binder ratio), and the binder ingredient type.

2.2 Used materials and mix design

As shown in Table 1, the mixing design of concrete is as follows: water binder ratio of 37, 42, and 47%; 2-ingredient type (50% OPC and 50% slag); 3-ingredient type (50% OPC, 35% slag, and 15% fly ash). Table 2 shows the materials used in this study. The admixture of OPC, ground granulated blast-furnace slag and fly ash was used as a concrete binder. Superplasticizer and AE agent were used to secure a certain consistency and air contents for concrete. River sand and crushed aggregate were used as aggregate.

2.3 Fundamental properties of concrete

Table 1 shows the basic physical properties of concrete. The ranges of slump and air contents of OPC, BFS50%, and BFS35%+FA15% at the water binder ratios of 37, 42 and 47% were 18.0~21.5 cm, 3.5~5.0%. The air contents of none AE OPC concrete were 2.5, 2.8 and 3.8% at the water binder ratios of 37, 42 and 47%. The compressive strength on the 28th day of standard curing differed with each mixing design (OPC > BFS50% > BFS35%+FA15%). It was measured at 45~50 Mpa, 43~45 Mpa, 39~41 MPa at the water binder ratios of 37%, 42% and 47%, respectively.

2.4 Test items and testing method

Photo 1 illustrates the method used to evaluate the frost durability of concrete caused by freezing-thawing. The test was performed in accordance with KS F 2456 (testing method for resistance of concrete to rapid freezing and thawing) and ASTM C666 (resistance of concrete to rapid freezing-thawing). During the freezing-thawing test, the first resonant frequency was measured every 30 cycles and the relative dynamic modulus for the dynamic modulus before the freezing-thawing test was calculated.[5)] At the end of 30 cycles, the underwater weight and surface-dry weight of the specimen were measured in order to quantitatively analyze the surface deterioration of concrete. Then the scaling amount (cm^3/cm^2) of concrete was measured using Equation (1).

$$Vsn = \frac{(Vo - Vn)}{A} \qquad \text{Equation (1)}$$

Table. 1. Mixing design and Fundamental Property of Concrete

Mix Classification	W/B (%)	S/a (%)	unit water content (kg/m^3)	Unit Weight (kg/m^3)							Superplasticizer (B×%)		Slump (cm)	Air content (%)	Strength at 28 days (MPa)	Freezing water
				B	C	Fa	S	F.A	C.A	CH.	SP	AE				
37OPC	42	45	168	454	400	-	-	764	948	-	1.20	None	21.5	2.5	50	Tab water
												0.025		4.7		Salt water
37BFS50					227	-	227	757	939	-	0.70	0.023	22.5	2.8	48	Salt water
37BFS35Fa15					227	68	159	748	928	-	0.60	0.030	21.5	3.6	45	Salt water
42OPC	42	45	168	400	400	-	-	784	973	0.3	0.70	None	19.0	2.8	45	Tab water
												0.015		4.7		Salt water
42BFS50					200	-	200	780	969	0.6	0.50	0.014	20.0	4.2	45	Salt water
42BFS35Fa15					200	60	140	773	959	1.2	0.45	0.014	18.0	3.5	40	Salt water
47OPC	47	47	168	357	357	-	-	835	956	-	0.60	None	18.5	4.7	41	Tab water
												0.013		4.7		Salt water
47BFS50					179	-	178	832	953	-	0.40	0.011	20.0	4.9	39	Salt water
47BFS35Fa15					179	54	125	825	945	-	0.40	0.012	20.0	4.5	40	Salt water

B: Binder, C: Cement, Fa: Fly ash, S: BFS, F · A: Fine Aggregate, C · A: Coarse Aggregate, CH.: Chloride,
SP: High Water Reducing Agent, AE: Air Entraining Agent

Table 2. Physical Properties of Used Materials

Materials	Physical Properties
Cement	• Ordinary Portland Cement(OPC) • Specific Gravity:3.16, • Fineness:3,214cm^2/g • Ig. loss:0.78, • Stability:0.06% • Initial setting time-2:36, • Final setting time-5:17
Blast Furnace Slag	• Specific Gravity:2.89, • Fineness:4,340cm^2/g • Ig. loss:0.59%, • Chloride ion:0.001%,
Fly Ash	• Specific Gravity:2.19, • Fineness:3,621cm^2/g • Ig. loss:3.29%, • Moisture volume:0.13% • SiO2 Volume:63%
Super-plasticizer	• High Water Reducing Agent • Naphthalene Type • Air entraining agent
Fine Aggregate	• Washing sand, • Specific Gravity:2.58, • Absorption ratio:1.01, • F.M.:2.89
Coarse Aggregate	• Crushed Gravel(25mm) • Specific Gravity:2.62, • Absorption ratio:0.82 • F.M.:6.87

where, V_{sn} : Scaling volume after n cycles (cm^3/cm^2)
V_o : Volume of specimens before freezing-thawing test (cm^3)
V_n : Volume of specimens after n cycles (cm^3)
A : Surface area of specimens before freezing-thawing test (cm^2)

The volume (cm^3) of the specimen was calculated using Formula (2).

$$Vn = (Wn - Wwn) \times \rho w \qquad \text{Equation (2)}$$

(a) Freezing-thawing testing machine (b) Evaluation of dynamic elasticity modulus

Photo 1. Resistance evaluation of concrete to freezing and thawing

where, V_n : Volume of specimens after n cycles (cm^3)
W_n : Surface drying weight after n cycles (g)
W_{wn} : Underwater weight after n cycles (g)
p_w : Specific gravity of water

3. Experimental results

3.1 Frost resistance of concrete with air contents

Fig. 2, respectively, show the results of evaluating the frost durability of none AE concrete and AE concrete at each water binder ratio of OPC-using concrete. In the case of none AE concrete, the rupture and relative dynamic modulus of the specimen were noticeably decreased, whether through tap water or seawater. The specimen frost-damaged by tap water showed a rupture without any sign of surface deterioration, while the specimen frost-damaged by seawater showed signs of rapid surface deterioration and of breaking and rupture. Especially in the case of the specimen under the freezing-thawing test at W/B

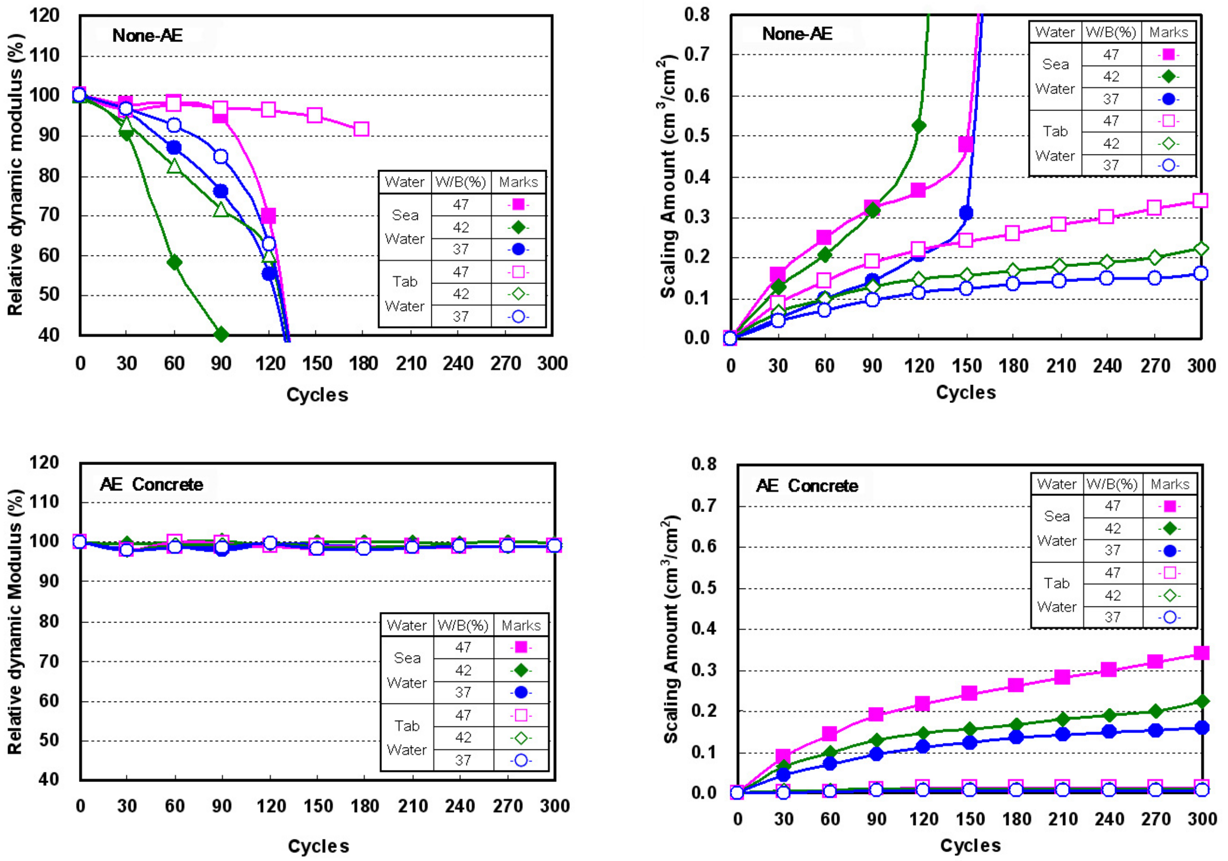


Fig. 2. Relative dynamic modulus and surface scaling amount of None AE Concrete and AE Concrete with freezing-thawing

of 47% using tap water, no rapid decrease of relative dynamic modulus was shown before 180 cycles, but at 180 cycles an abrupt rupture occurred, making further measurements impossible.

Therefore, it has been confirmed that in the case of none AE concrete frost-damaged by seawater, deterioration occurs simultaneously inside and outside the concrete and the durability rapidly decreases.

Meanwhile, in the case of AE concrete, whether with tap water or seawater, the relative dynamic modulus, proving to have excellent durability, showed little change before and after frost-damage,. But, surface deterioration was more noticeable in the specimen frost-damaged by seawater than that frost-damaged by tap water. The surface deterioration of concrete frost-damaged by seawater was reduced by increasing the strength of concrete and securing appropriate air contents using AE agent.

3.2 Frost resistance of concrete with W/B and binder types

Figs. 3 and Fig. 4, respectively, show the results of evaluating the relative dynamic modulus and surface deterioration of concrete frost-damaged by seawater at each water binder ratio and binder mixing method. At W/B of 37%, the change of relative dynamic modulus was more noticeable when using seawater than tap water. This is thought to be because, when concrete is frozen, the surface deterioration of concrete is more accelerated, along with erosion by seawater. In the cases of the specimens under the freezing thawing test at W/B of 37% OPC-seawater and W/B of 42% OPC-tap water, the relative dynamic modulus' were measured at 60% and 75%, respectively. All specimens except for these showed a relative dynamic modulus of over 95%.

Fig. 5 shows the results of evaluating the surface deterioration of concrete at each water binder ratio and according to freezing water. The surface scaling amount was larger when freezing-thawing was caused by seawater than by tap water. This is thought to be because the freezing expansion pressure on the concrete surface exercises greater influence in the case of seawater than that of tap water.

As a result of evaluating the scaling amount at each binder ratio, OPC concrete showed a great difference in the amount of scaling through tap water as opposed to

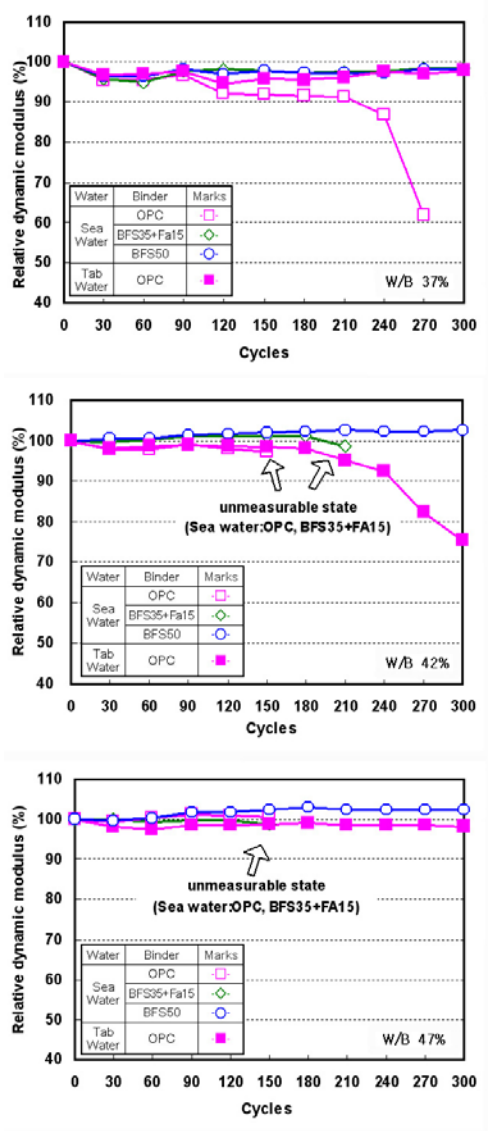


Fig. 3. Relative dynamic modulus

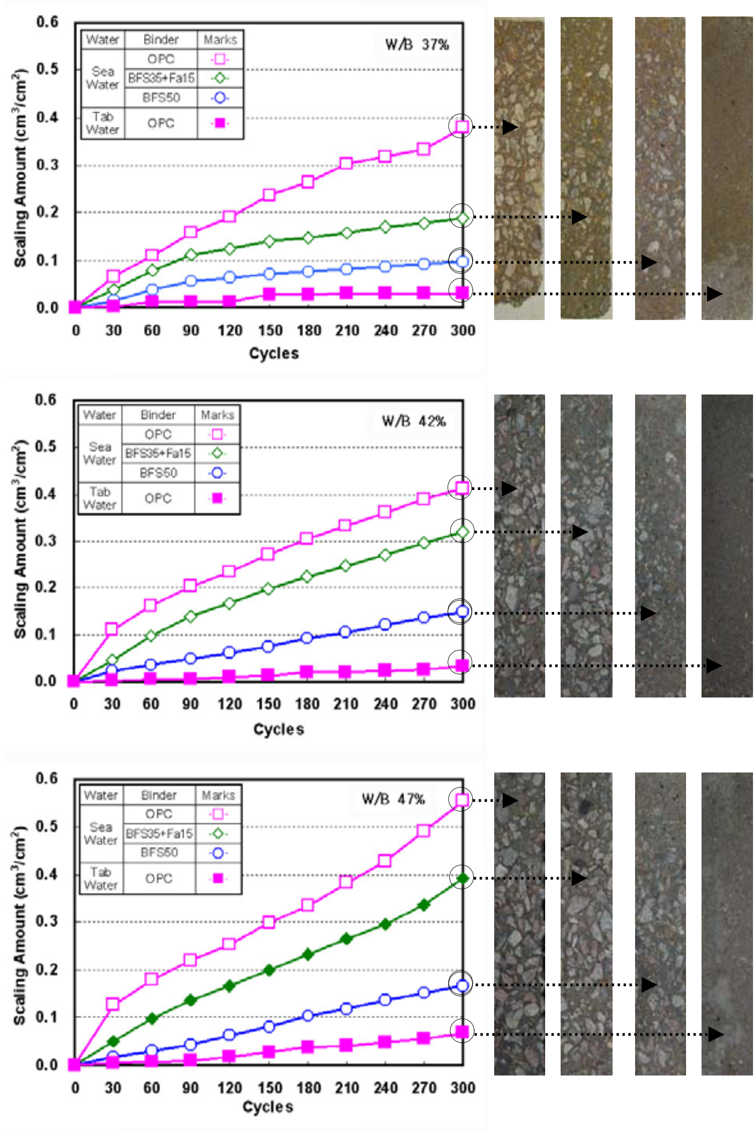


Fig. 4. Surface scaling amount

seawater.

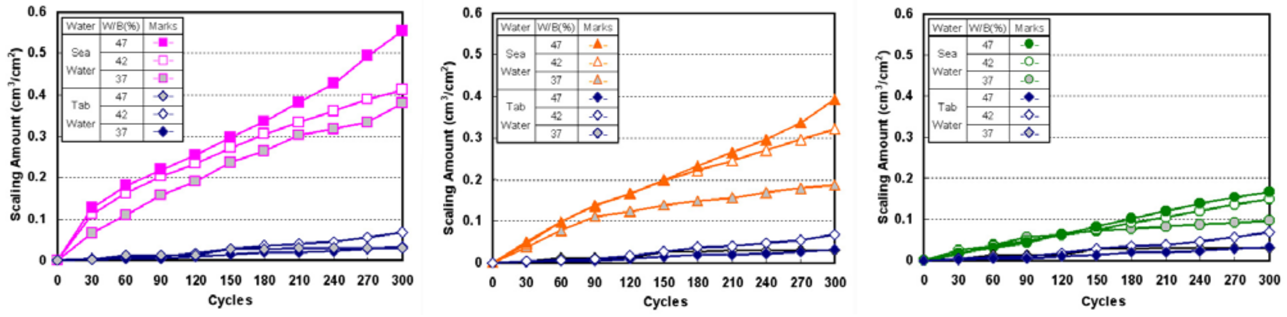
In evaluating the frost durability of concrete, except for the fact that the freezing-thawing specimen at W/B of 42% OPC-tap water showed a slight decrease in relative dynamic modulus, the relative dynamic modulus by tap water and seawater didn't show any distinct trend. As well, it has been confirmed that the surface deterioration of concrete is greatly affected by seawater.

The scaling amount of concrete according to binder ratio showed the following order: OPC>BFS35%+FA15%> BFS 50%. Two-ingredient type and 3-ingredient type concrete showed a relatively higher surface deterioration resistance compared to OPC concrete. Binder ingredient type has a more distinct effect than the reduction of water binder ratio. BFS 50% concrete is the most effective for deterioration by seawater. This is thought to be because slag, through fixing of chloride, reduces the deterioration of concrete by chloride.

In the future, therefore, the utilization of slag is recommended for marine concrete structures that are subject to decreased durability due to salt damage by seawater, e.g. sea-salt aerosols and droplets.

Photo 2 shows the surface scaling of W/B 42% OPC concrete in the case of freezing water. Surface deterioration was more noticeable through freezing-thawing by seawater than through tap water.

The fact that the scaling amount by seawater freezing-thawing becomes greater in spite of a similar relative



(a) OPC Concrete (b) BFS 35%+FA 15% Concrete (c) BFS 50% Concrete

Fig. 5. Surface scaling amount of concrete with binder types

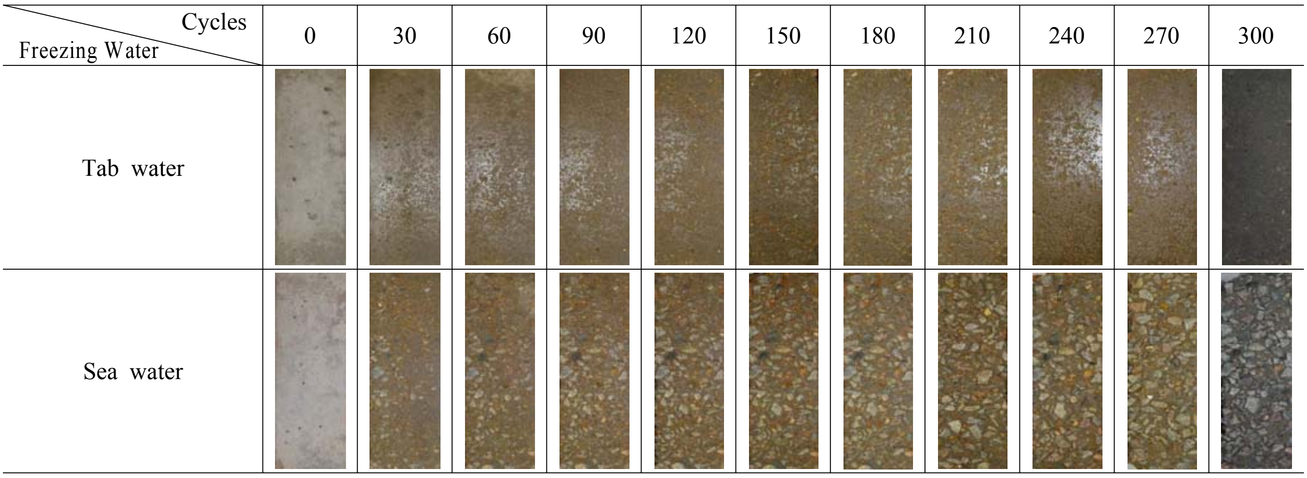


Photo 2. Surface scaling with freezing water (W/B 42% OPC Concrete)

dynamic modulus is largely due to the noticeable scaling caused by destruction of the fine structure on the concrete surface. This is thought be, as shown in Photo 3, because the freezing of the moisture inside concrete with inherent chloride decreases the stability of the fine porous structure and thus increases the osmotic pressure.

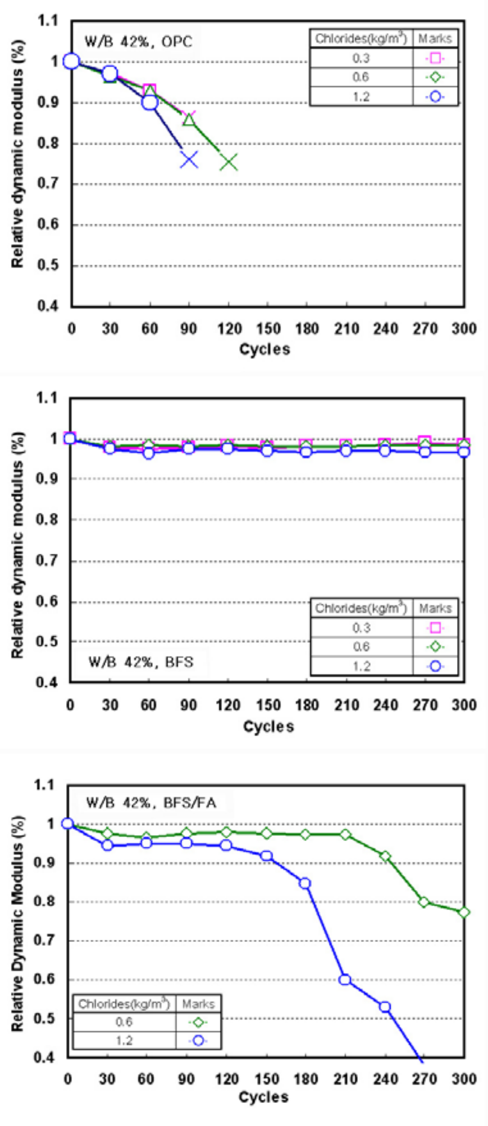
In the case of freezing-thawing of concrete with inherent chloride, a fine crack occurs inside the concrete, accelerating the decrease of dynamic modulus and the diffusion of chloride, and eventually causing a combined deterioration through frost damage and salt damage.

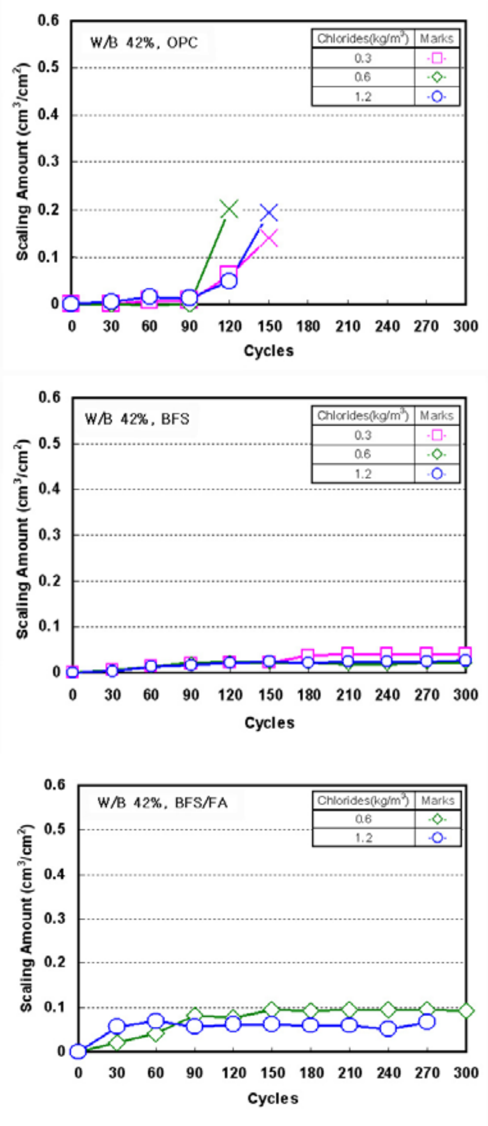
3.3 Deterioration of concrete with inherent chloride

Figs. 6 and 7 show the results of evaluating the frost durability and surface deterioration of concrete with inherent chloride. Contrary to the surface deterioration of concrete frost-damaged by outside seawater, surface deterioration rarely occurs in cases of concrete containing chloride inside, but its internal structure is rapidly destroyed, thus decreasing its frost durability. Therefore, it has been confirmed that chloride inside concrete is the fundamental cause of a decrease in structural safety by erosion of the reinforcement, and that it triggers an abrupt decrease of resistance to frost damage.

As a result of evaluating its relative dynamic modulus and surface deterioration, BFS 50% concrete was found to be rarely subject to frost damage. BFS mixed into concrete has the effect of decreasing the action of chloride so that, even though chloride is inherent inside concrete, this does not bring about a rapid decrease of durability, as in OPC concrete. BFS is judged to have the effect of reducing the expansion by chloride inherent inside concrete.

Mixing chloride of 0.6 and 1.2 kg/m^3 into 3-ingredient concrete (BFS35+Fa15) showed that the decrease of durability was more noticeable than when it was mixed into slag 50% concrete. But it is judged to have a greater effect of hampering the decrease of durability. Therefore, BFS, a component of 3-ingredient concrete, is recognized as having the effect of reducing the expansion by chloride, but FA is not.





Inherent chlorides
0.3 kg/m³ 0.6 kg/m³ 1.2 kg/m³

Chlorides (kg/m³)
0.3 0.6 1.2

Chlorides (kg/m³)
0.3 0.6

Fig. 6. Relative dynamic modulus

Fig. 7. Surface scaling amount

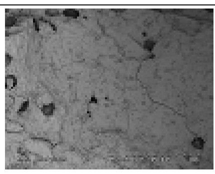
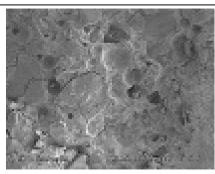
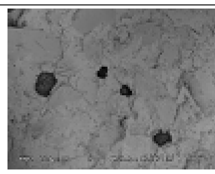
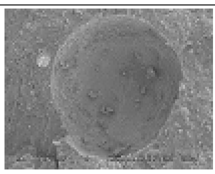
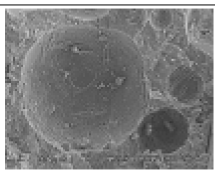
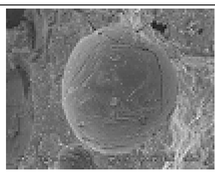
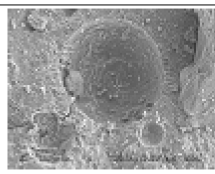
magnification	Base-OPC (Before freezing-thawing)	Tab water-OPC	Sea water-OPC	Sea water -BFS35%+FA15%	Sea water-BFS 50%
× 50					
× 250					

Photo 3. The fine structure on the concrete surface (300 cycles)

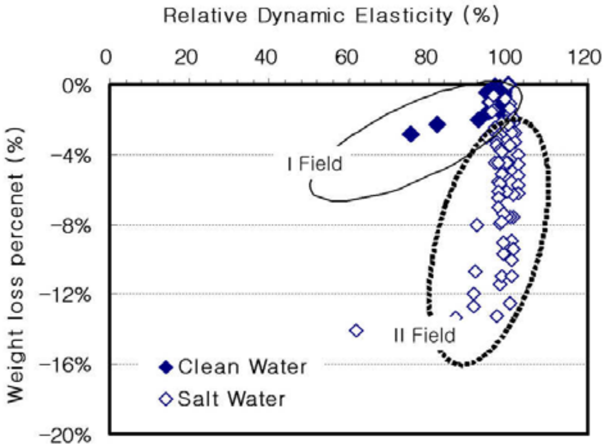


Fig. 8. relationship between relative dynamic modulus and scaling amount

Table 3. surface deterioration resistances (Freezing-thawing 300cycles, Scaling amount (cm³/cm²))

W/B (%) \ Binder types	BFS 50%	BFS35%+ FA15%	OPC
37	26	50	100
42	36	79	100
47	33	73	100

Table 4. the stages of scaling of concrete based on the scaling amount (cm³/cm²)

Stages	Ⅰ	Ⅱ	Ⅲ	Ⅳ	Ⅴ
Scaling amount / Base Specimen	0~0.1	0.1~0.2	0.2~0.3	0.3~0.4	Over 0.4
					
Surface soundness	Mortar surface scaling	Aggregate exposure	Aggregate over exposure	Sectional breaking	Rupture

3.4 Evaluation method of surface deterioration due to cyclic freezing and thawing

Fig. 8 shows the relationship between relative dynamic modulus and scaling amount. As a result of frost durability evaluation based on relative dynamic modulus, the concrete used within the scope of this study was evaluated as a high-durability concrete since it has a low water binder ratio and an appropriate amount of entrained air. But the surface deterioration of concrete by seawater had a wide range of change regardless of relative dynamic modulus, and didn't show any special correlation.

There are two distinct areas: Area I, where dynamic modulus decreases by freezing-thawing of tap water, and Area II, where scaling deterioration decreases by freezing-thawing of seawater. In the case of concrete in an environment subject to decrease of durability by seawater, this is through a combined deterioration of dry-wet repetition and freezing-thawing by seawater, so it requires not only a standard evaluation of frost durability based on relative dynamic modulus but also an evaluation of the deterioration of the concrete surface.

Table 3 shows the surface deterioration resistances of BFS50% and BFS35%+ FA15% concretes, based on the degree of surface deterioration of OPC concrete at 300 cycles of seawater freezing-thawing being 100.

Table 4 suggests the stages of scaling of concrete based on the scaling amount measurement result. The surface deterioration of concrete goes through the following stages: mortar surface scaling < aggregate exposure < aggregate overexposure < sectional breaking < rupture. It is thought that the scaling amount (cm³/cm²) of concrete can be utilized as an index to the degree of surface deterioration.

4. Conclusion

It has been confirmed that the decrease of concrete durability was much more noticeable in a chloride-supplying environment than in a general environment. And, when concrete is subjected to freezing and thawing in a chloride-supplying environment, we confirmed that deterioration of concrete increases.

(1) In the case of concrete with an appropriate amount of entrained air, the frost durability was shown to improve compared to concrete with a smaller amount of entrained air. The durability was shown to decrease more rapidly in combined deterioration through salt damage and frost damage than in a single deterioration.

(2) The frost durability and surface deterioration resistance of blast-furnace slag-mixed concrete were evaluated as higher than OPC concrete. BFS50% concrete showed a better effect of reducing chloride penetration, compared to BFS35%+FA15% concrete. This can be effective for improving the durability of concrete structures subject to salt damage.

(3) It has been confirmed that the quantitative analysis

of the amount of scaling, calculated from concrete's underwater weight and surface-dry weight affected by the freezing-thawing of seawater, is valid as a method of evaluating concrete surface deterioration.

Acknowledgments

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