

Basic Research on Frost Resistance of LPC-FA Concrete Placed in Chloride Environment

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Abstract—In cold regions in the world, the deterioration of a concrete such as scaling and pop-out is caused by freezing and thawing action. Furthermore, the compounding with salt damage, carbonation and the like has a major influence on the durability and the appearance of the concrete structure. Deterioration resistance generally improves with densification. In this study, we evaluated the frost damage resistance of concrete using low heat portland cement and fly ash (LPC-FA concrete). In the compounding in which the strength property and the air voids structure change with the material age, it conducted various tests. As a result of compressive strength, it was confirmed that it had sufficient strength regardless of W/B and air. Although the exposed specimens were subjected to more than 300 freeze-thaw cycles, high strength was confirmed. For this reason, it is exposed that the influence of the freeze-thaw action under the actual environment is small. In the early material ages, the scaling amount was higher as W/B was larger and air was smaller, similar to the general tendency. On the other hand, with the material age, the resistance was greatly improved, and at 365 days curing, it became 0.25 g/cm² or less in all the mix proportions, and no correlation by air was observed. Therefore, it is expected that the influence of the expansion pressure is small and influence of the osmotic pressure due to chloride ions or the like is large. In conclusion, LPC-FA concrete is considered to have sufficient practicality.

Index Terms—frost damage, low heat portland cement, fly ash, air voids structure, compressive strength

I. INTRODUCTION

Concrete structures and concrete products are strictly controlled to use materials, mix proportions, curing, construction and the like so as to have predetermined quality and performance. However, in cold regions where the temperature is below freezing, surface deterioration such as scaling and pop-out is sometimes observed due to freezing and thawing action. Furthermore, the compounding with salt damage, carbonation and the like has a major influence on the durability and the appearance of the concrete structure [1].

Since these deteriorations progress from the surface, the degree of deterioration tends to be small if the strength property and the mass transfer resistance of the surface layer are favorable. The concrete surface layer has a role as a protective layer to prevent external

deterioration factors entering the inside, and is a very important part for enhancing deterioration resistance.

In order to improve the resistance to deterioration of concrete, it is necessary to densify the surface layer. It is known that these concretes become very high resistance to deterioration by curing long term [2]. In particular, concrete using fly ash degrades in response to changes in void structure due to material age, such as the transition zone that becomes coarse voids with a diameter of 50nm or more because the pozzolanic reaction continues over several years resistance also changes [3].

Deterioration resistance generally improves with densification. However, the resistance of frost damage may be reduced in terms of expansion pressure and osmotic pressure [4].

II. OUTLINE OF EXPERIMENT

A. Materials Used and Mix Proportion

1) Design policy

In this study, concrete using low heat portland cement and fly ash (LPC-FA concrete) was taken as a cement matrix with large changes in strength property and void structure on material age. The used materials and the mix proportions were designed in consideration of strength development, physical and chemical performance, suppression of cracks, and workability so that effects other than void structure change are minimized. The design principal of the materials used and the ingredients are shown in Table I.

TABLE I. DESIGN PRINCIPAL

Characteristic	Policy
Strength expression	Increase compressive strength
Physical and chemical performance	Reduce permeability and diffusivity
	Set appropriate congelation time
	Use chemically stable materials
	Reduce the large air voids and densify
Crack control	Suppression of heat of hydration
	Suppression of drying shrinkage
	Suppression of self-contraction
Workability	Increase flowability and material separation resistance

2) Materials used

The materials used were a relatively easily available material. As the binder, low heat portland cement and fly

ash were added with super plasticizer and limestone fine powder in consideration of self-filling property so that there was no difference in the quality of the specimens due to the factors at the concrete placing. Also, in order to eliminate the influence caused by the aggregate as much

as possible, the materials other than the binder were unified with the materials based on chemically stable limestone. An outline of the materials used is shown in Table II.

TABLE II. OUTLINE OF THE MATERIALS

Material, Name	Code	Note
Low heat portland cement	LPC	Density=3.24g/cm ³ Specific surface area=3730cm ² /g
Fly ash	FA	Density=2.17g/cm ³ JIS type II, Specific surface area=3610cm ² /g
Limestone fine powder	LS	Density=2.70g/cm ³ Specific surface area=5250cm ² /g
Sand : Lime crushed sand	S	Density=2.66g/cm ³ Hachinohe Matsudate Production, FM=2.79
Gravel : Lime crushed stone	G	Density=2.69g/cm ³ Hachinohe Matsudate Production, FM=6.63
Admixture : Air entraining and high range water reducing admixture, Air amount regulator	SP	Carboxyl group-containing polyether compound
	AS	Polyalkylene glycol derivative

3) *Mix proportion*

The mix proportion was based on LPC-FA concrete with the water binder ratio of 45%, which has execution of workability test in previous studies [5] [6]. The water binder ratio was set to 60% and 75% to make a clear difference in pore structure. In addition, the unit amounts

of water, powder and aggregate were adjusted so that the fresh property would not cause harmful materials separation, and the slump flow would have the same ratio within the range satisfying the standard. The mix proportion of the specimens is shown in Table III.

TABLE III. MIX PROPORTION

W/B (%)	Gmax (mm)	s/a (%)	Slump flow (cm)	Air (%)	Unit amount (kg/m ³)								
					W	Powder : P		S	G	SP	AS		
						Binder : B							
						LPC	FA						
45	20	53.4	65±5.0	2.5	160	249	107	178	883	780	0.95	/	
				5.0									0.060
				7.5									0.150
60	20	53.4	65±5.0	2.5	156	186	80	265	886	780	0.95	0.005*	
				5.0								0.060	
				7.5								0.030	
75	20	53.4	65±5.0	2.5	155	148	64	318	887	780	0.95	0.015	
				5.0								0.015	
				7.5								0.090	

* Defoamer

B. *Experimental Method*

1) *Specimens*

The concrete was mixed in a mixing amount of about 20 to 50 liters per batch and the mixing time for 120 seconds by a twin screw forced mixer. Each mix proportion was placing concrete in two batches of 100×100×400mm, 100×500×400mm, φ100×200mm.

The amount of air was adjusted to be approximately 2.5%, 5.0%, 7.5% depending on the amount of admixture added, and the slump flow was confirmed to be 65±5.0cm. The prepared specimens were demolded at 1 day of material age, and after curing water for 28 days, 91 days, 365 days in constant temperature curing tank (20°C) respectively, they were subjected to various tests.

2) *Experimental item*

In the experiment, the Compressive strength was measured to obtain an general indicator, and a Scaling test and Electrophoretic diffusion test based on deterioration in a chloride environment was performed. Moreover, in order to obtain the index of the air voids structure, manual linear traverse method was carried out. They based on various standards. The test items and methods are as follows.

- Amount of air : Method of test for air content of fresh concrete by pressure method (JIS A 1128)
- Air content of hardened or Air voids spacing factor : Manual linear traverse method (ASTM C 457)
- Compressive strength : Method of test for compressive strength of concrete (JIS A 1108)
- Scaling : Scaling test (RILEM CDF method)
- Effective diffusion coefficient : Test method for effective diffusion coefficient of chloride ion in concrete by migration (JSCE G571)

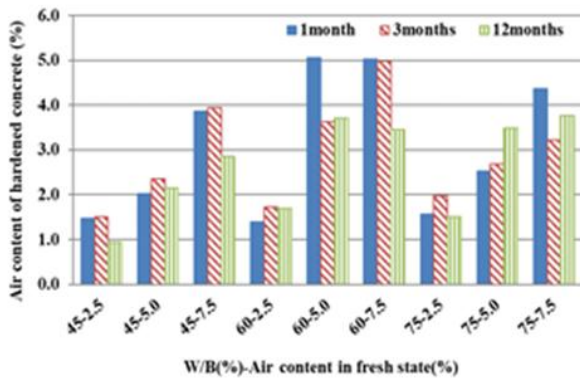


Figure 1. Air content of hardened concrete

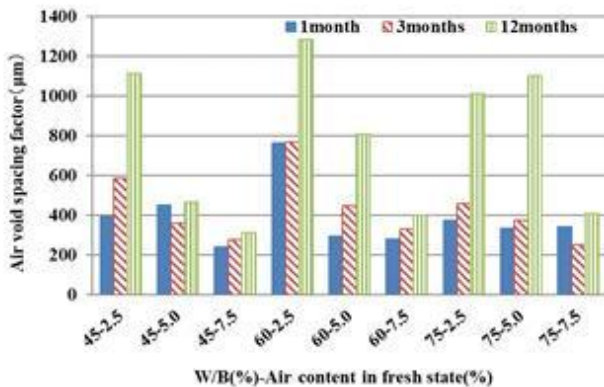


Figure 2. Air void spacing factor

III. EXPERIMENTAL RESULTS AND CONSIDERATION

A. *Air Content of Hardened and Air Voids Spacing Factor*

1) *Air content of hardened*

The amount of air of each mix proportions measured using the linear traverse method is shown in Fig. 1. The air content was about 2/3 of the air content of air at the time of freshness. In addition, the values were almost the

same for each mix proportions regardless of the curing period. This is considered to be due to the fact that the influence of densification is not reflected, since the measurement of the amount of air by the linear traverse method cannot measure the pore diameter of about 10µm or less.

2) *Air voids spacing factor*

The air voids spacing factor of each mix proportions measured using the linear traverse method is shown in Fig. 2. It was generally similar to the general tendency, and was smaller as the amount of air was larger. Moreover, while the material age is the same value until 91 days curing, the sample of five cases out of the 9 cases becomes about twice at 365 days curing.

The specimens with doubled the air voids spacing factor tended to have a relatively small amount of air. However, no change was found in the specimens with an air content of about 7.5% when fresh.

There was almost no difference in air volume with material age, but a clear difference was observed in the air voids spacing factor. All the specimens with doubled the air voids spacing factor had small amounts of air (generally less than 3.0%) and small amounts of addition of air amount modifiers (about 0.2 kg/m³ or less).

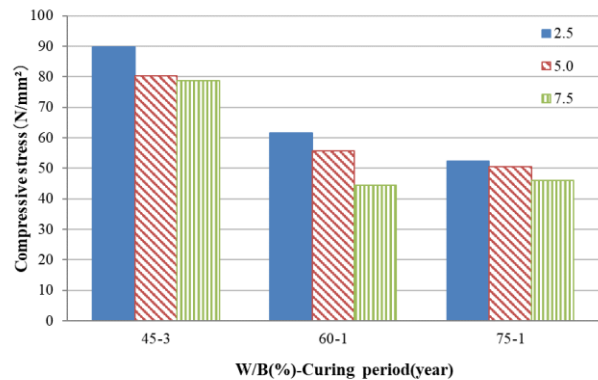


Figure 3. Compressive strength (water curing)

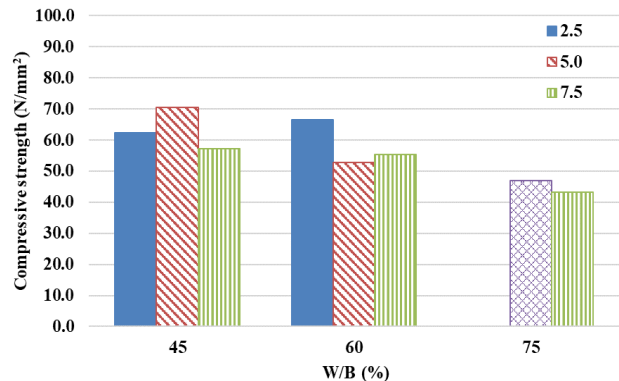


Figure 4. Compressive strength (exposed specimens)

Therefore, the introduction amount of entrained air (about 30 to 250µm) is expected to be small. In the case where the number of small bubbles is extremely small, when one bubble disappears, the influence on the air voids spacing factor is large. From this, it is considered that the air voids spacing factor is significantly increased because in the cases of the specimens with a small

amount of air, the voids of the minute bubble diameter which can be measured by the progress of the pozzolanic reaction during the curing period of 365 days, so the range of influence on the air amount is minute.

B. Compressive Strength

The results of the compressive strength test of the specimens cured in water for 1 year and 3 years are shown in Fig. 3, and the results of the exposed specimens cured in air for three years are shown in Fig. 4. For exposed specimens, it is 3.8% and 7.5% due to the air volume adjustment. Although visual observation was not possible, no cracks were observed.

As a result, the strength in the case of one-year water curing and the strength in the case of three-years air curing were close to each other, and there was not much difference due to the mix proportions. At W/B 75%, the strength tends to be somewhat low, but still 40 to 50 N/mm² is secured. From Fig. 4, the strengths of W/B 45% and 60% were about 60 N/mm², which was comparable, and no correlation was found with the air amount.

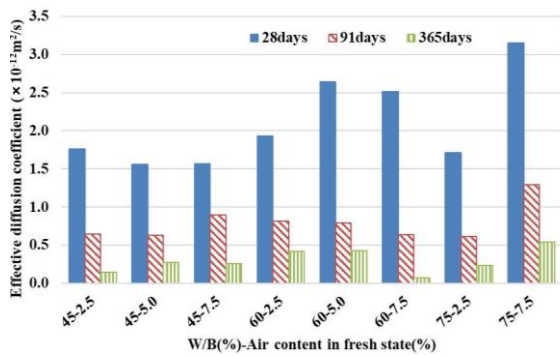


Figure 5. Scaling amount

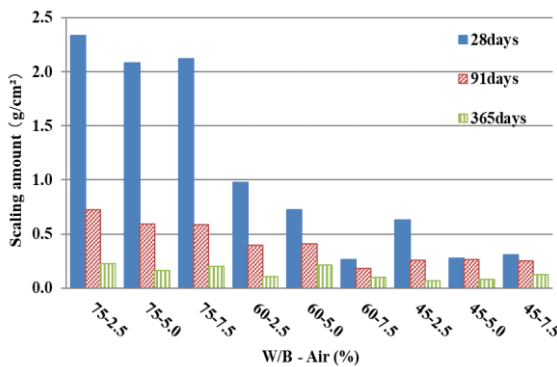


Figure 6. Effective diffusion coefficient

Here, it is 10950°C when calculating the integrated temperature at 1-year material age of the specimens cured in water. Next, based on the data of the Japan Meteorological Agency, the accumulated temperature of the exposed sample was about 12580°C, and no clear difference was observed. And, the number of cycles subjected to the freeze-thaw action was about 330 times. In previous studies, in the freeze-thaw test, specimens cured in water for 1 year tended to break W/B 75% and Air 2.5% specimens at 150 cycles, but exposed

specimens of all had sufficient strength [7]. In addition, it is expected that about 50m³ of water was supplied from the amount of precipitation. It can see that this is extremely small compared to the water curing supply.

From these, it is considered that the difference depending on the curing method is not due to the accumulated temperature or the freeze-thaw action, but because the water supply necessary for the pozzolanic reaction is not sufficient. About this, since it is estimated that strength will be developed with water supply by precipitation in the future, observation will be continued until the curing of 5 years.

C. Scaling

In the amount of scaling at the end of 50 cycles is shown in Fig. 5. Finally, the cement paste portion was peeled off and the unevenness was noticeable in all specimens.

The scaling amounts at the end of 50 cycles are compared. First, at 28 days curing, at W/B 45%, Air 2.5% was 0.63 g/cm², Air 7.5% was 0.31 g/cm², and the larger the amount of air, the higher the scaling resistance, and to some extent the overall it showed a small tendency. At W/B 75%, Air 2.5% was 2.33 g/cm², Air 7.5% was 2.12 g/cm², and it was confirmed that the scaling resistance was remarkably low regardless of the air amount.

Next, at 91 days curing, Air 2.5% was 0.26 g/cm² and Air 7.5% was 0.25 g/cm² at W/B 45%. The tendency to improve from 28 days curing was confirmed, and the correlation with the amount of air has disappeared. In addition, at W/B 60% and W/B 75%, the tendency to significantly improve scaling resistance was confirmed, and at W/B 60%, Air 2.5% was 0.39 g/cm² and Air 7.5% was 0.18 g/cm². At 91 days curing W/B 60%, the scaling amount was about the same as 28 days curing W/B 45%.

In addition, at 365 days curing, W/B 45% and W/B 60% were extremely small, about 0.1 g/cm² and even W/B 75%, to about 0.2 g/cm². Significant improvement in scaling resistance was confirmed in all the mix proportions regardless of the air content.

From these results, it is considered that LPC-FA concrete has improved resistance to deterioration by densification of the structure in the pozzolanic reaction of fly ash. This is considered to be a result showing that the decrease in the amount of void due to the densification of the internal structure does not necessarily lead to the decrease in scaling resistance.

Furthermore, although the exposed specimens are in an environment where there is no supply of chloride ions, the number of freeze-thaw cycles is about 330 times, which is more than six times. However, since no deterioration due to scaling was observed in visual inspection, it is considered that the influence of chloride ions is largely exerted.

From now on, I will carry out the scaling test (RILEM CDF method) also for exposed specimens.

D. Effective Diffusion Coefficient

The effective diffusion coefficient of each mix proportions measured by the Electrophoretic diffusion

test is shown in Fig. 6. The effective diffusion coefficient was on the order of 10^{-12} m²/s in all cases up to 28 days curing, and in the cases of 91 days curing, they are on the order of 10^{-13} m²/s except for the specimen of W/B 75% and Air 7.5%.

IV. CONCLUSIONS

In this study, the deterioration resistance of LPC-FA concrete was evaluated by various tests, and the tendency of the physical property change according to the material age was confirmed. The results obtained are as follows.

- The air content at the time of freshening decreased to about 2/3 after hardened, and then it did not change until the 365 days curing.
- The air voids spacing factor, some cases doubled from 91 days to 365 days curing were also found.
- Compressive strength, no difference due to W/B was observed, and it was confirmed that W/B 75% had sufficient strength.
- The scaling amount, significant improvement of deterioration resistance was confirmed in long-term material age.
- The effective diffusion coefficient, the penetration of deterioration factor from the outside was sufficiently small regardless of the mix proportions when the curing period was 365 days.

From these results, densification of the structure is important for measures to reduce deterioration of frost damage under a chloride environment. It is considered that LPC-FA concrete in which the pozzolanic reaction has sufficiently progressed after an appropriate curing period has sufficient practicability.

In the future, I plan to evaluate and examine the mass transfer resistance by the RILEM CDF method and the Electrophoretic diffusion test, and the void structure by the Manual linear traverse method and the Mercury injection method, for the exposed specimens which gave good results in the compressive strength test.

CONFLICT OF INTEREST

A part of this research was conducted in response to a research grant from a research or activity related to the maintenance and maintenance of social infrastructure in fiscal 2018.

AUTHOR CONTRIBUTIONS

Shogo Kawamorita analyzed the collected data and wrote a draft manuscript. Dr. Kazuhito Niwase built the research concept and design, critical revision of the article for important intellectual content.

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contain radioactive waste and the development of super durable concrete. He received a paper award from the Japan Concrete Institute, which was awarded to the author for a paper recognized as having made a significant contribution to the progress of academic and technological progress in concrete.