Influence of carbonation and freeze-thaw on macro-properties of concrete

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Abstract. Concrete can be damaged under the effects of carbonation and the freeze-thaw cycle, which is a common cause of premature failure for concrete structures. In this study, range analysis was performed for compressive strength results after carbonation and freeze-thaw cycles for 90 days. A carbonation test, freeze-thaw test, and the alternating cycle of carbonation and freeze-thaws were performed to measure the relative dynamic elastic modulus and flexural strength of concrete samples. The results showed that specimens subjected to thawing first, then carbonation suffered the greatest impairment to strength due to expansion and osmotic pressures caused by water motion after thawing; this caused some of the original closed pores to link together, which loosened the internal organization and increased total porosity. The dynamic elastic modulus loss and weight loss of carbonized specimens were smaller than those of uncarbonized specimens within a reasonable range of carbonation. The flexural strength carbonation declined as the water-binder ratio or fly ash content increased.

Keywords: carbonation, freeze-thaw, macro-properties, fly ash.

1. Introduction

Concrete is the most common building material over the world [1-3]. Hydraulic concrete durability is one of the most important factors in the field of concrete studies because the performance and lifespan of many projects depend on concrete durability. Modern dams adopt a series of durability protection measures. Due to diversity of the application conditions and complexity of the concrete system itself, the durability problem of hydraulic concrete still exists; therefore, further discussion regarding hydraulic concrete, damaged caused by carbonation /freeze-thaw, and prevention measures are necessary [4-5]. In the 1960s, some developed countries began to focus on concrete durability, and a large number of experimental studies and theoretical analyses were conducted on concrete carbonation. Researchers have come to a relatively unified understanding of concrete carbonation mechanisms [6]. The influencing factors of concrete carbonation, artificially accelerated carbonation, and carbonation depth detection have been discussed. Concrete carbonation research has entered the molecular level, and the model for carbonation depth and life prediction under a single carbonation is relatively well developed. In recent years, multiple degradation factors on concrete durability are becoming more and more important among researchers [7]. As for hydraulic concrete, carbonation and freeze-thaw cycles are the most prominent factors. Currently, the study of single factor freeze-thaw or carbonation cycles are mature, but theoretical research of concrete durability under alternative freeze-thaw and carbonation cycles is not mature [8].

Concrete undergoes changes in macrostructure when it suffers carbonation and freeze-thaw cycles. In this study, carbonation, relative dynamic elastic modulus, mass loss rate and flexural strength were measured. Therefore, information that can lead to improving concrete performance under harsh carbonation and freeze-thaw cycles can be very beneficial.

2. Experimental

2.1. Raw materials

Chemical and physical properties of materials are listed in Table 1.

Table 1. Chemical, physical properties of materials.

	Chemical composition/%										Physical promerites	Compressive strength of cement/MPa	
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	R_2O	SO_3	loss	Specific density /(kg/m^3)	7 d	28d
Cement	22.5	3.8	4.8	63.0	2.1	0.50	0.1	0.4	2.1	0.7	3120	25.4	45.1
Fly ash	52.4	24.0	9.4	3.2	1.2	—	—	—	0.7	2.3	2380	—	—
Slag	33.6	14.6	1.7	34.7	9.9	0.7	0.3	—	2.0	2.4	2860	—	—

2.2. Orthogonal experiments

The freeze-thaw, carbonation and content of fly ash were viewed as the main factors of experiment to study the composite action of freezing-thaw and carbonation on compressive strength of cement mortar. Due to the water-cement ratio was an important factor determining the concrete performance, which had a significant impact for concrete strength, durability, and workability. Thus the water-cement ratio (C), content of fly ash (F), carbonation time (B), and freeze-thaw times (T) were four relatively important elements as factors of the orthogonal experimental design. Table 1 showed the factors and levels, each factors in three levels. The cement mortar was cured for 90 days and measured its compressive strength after alternating action of carbonation and freeze-thaw.

Table 2. Factors and levels.

Level	Factors			
	C(W/C)	F(Content of fly ash)/%	B(Carbonation time)/d	T(Freeze-thaw times)/times
1	0.4	0	3	20
2	0.45	20	7	50
3	0. 5	50	14	100

According to the four factors with three levels as shown in Table 2, select L9 (34) orthogonal design table for test. The test was mainly on alternating action of carbonation and freeze-thaw impact on concrete durability. The test was divided into two parts, one was carbonation after freeze-thaw, and the other was freeze-thaw after carbonation.

2.3. Freeze-thaw test and carbonation test

Two graded aggregate concrete with six mix proportions, twelve group tests are chosen for the test. The specimen is conducted carbonation test followed by freeze-thaw test or freeze-thaw test followed by carbonation test. The test scheme is listed in Table 3 and Table 4. The air content of concrete is controlled between 4.5% and 5.0%, the collapsed slump is controlled between 50 mm to 70 mm and the mix proportion is shown in Table 4. Due to a larger number of test pieces, a standard curing age is 28d. Mix proportions are shown in Table 5.

Table 3. Freeze-thaw after carbonation.

Specimen	W/C	FA(%)	Curing Age (d)	Carbonation (d)	Freeze-thaw times
B1	0.35	0	28	14	100
B2		20			
B3	0.45	20	28	14	100
B4		40			
B5	0.55	20	28	14	100
B6		40			

Table 4. Carbonation after freeze-thaw.

Specimen	W/C	FlA (%)	Curing Age (d)	Freeze-thaw times	Carbonation (d)
T1	0.35	0	28	100	14
T2		20			
T3	0.45	20	28	100	14
T4		40			
T5	0.55	20	28	100	14
T6		40			

The molding number in each group is six. The specimen size is 100mm×100mm×400mm. After curing in standard curing room for a scheduledtime, three piece were transplanted into a closed carbonation box, then into a freezing and thawing box after accelerated carbonation for 28d. Measure the quality and relative dynamic elastic modulus, both before and after being transplanted into the freeze-thaw box for 100 times. At last measure the depth of carbonation. The other three pieces did freeze-thaw test first, and suffered from accelerated carbonation for 28d. Do the carbonation test according to Test Code for Hydro-concrete(DL/T 5150—2001). The specimens should be taken out from the standard curing room before two days of the standard curing age, then measure the depth of carbonation after drying at 60 ℃± 2 ℃ for 48h. Specimen B1 to B6 are conducted carbonation test after freeze-thaw test. Specimen T1 to T6 are conducted freeze-thaw test after carbonation test.

Table 5. Mix proportion of specimen.

Specimen	Gradation	W/C	FA (%)	Aggregate ratio (%)	Admixture		materials(kg/m^3)			Slump (mm)	Air content (%)
					PCA (%)	GYQ (%)	water	Middle stone	Small stone		
B1/T1	two	0.35	0	30	0.48	0.012	117	813	665	55	4.5
B2/T2	two	0.35	20	30	0.45	0.011	117	806	659	62	4.7
B3/T3	two	0.45	20	30	0.43	0.011	117	833	682	65	5.2
B4/T4	two	0.45	40	30	0.43	0.011	116	829	678	65	4.9
B5/T5	two	0.55	20	30	0.42	0.010	117	850	696	69	4.8
B6/T6	two	0.55	40	350	0.42	0.010	116	847	693	70	4.6

2.4. Dynamic elastic modulus

According to former research, the relative dynamic elastic modulus is usually calculated as follows

$$P_n = \frac{f_n^2}{f_o^2} \times 100 \quad (1)$$

P_n: relative dynamic elastic modulus after n-th time of freeze-thaw cycle %
f_0: the natural frequency before freeze-thaw (Hz)
f_n: the natural frequency after n-th time of freeze-thaw cycle(Hz.)

3. Results and analysis

3.1. Strength range analysis after carbonation and freeze-thaw

Range analysis was done for compressive strength results after carbonation and freeze-thaw for 90 days. Table 6 and Figure 1 showed the results of range analysis

Table 6. Range analysis (freeze-thaw after carbonation).

Specimen	C	F	B	T	Compressive strength in 90d(MPa)
S1	1	1	1	1	37.1
S2	1	2	2	2	49.4
S3	1	3	3	3	41.5
S4	2	1	2	3	46.3
S5	2	2	3	1	38.1
S6	2	3	1	2	36.3
S7	3	1	3	2	34.8
S8	3	2	1	3	50.6
S9	3	3	2	1	48.9
(K1)	127.3	120.9	121.5	123.6	
(K2)	119.2	136.6	144.1	123.9	
(K3)	139.4	126.1	117.2	138.6	
[$K1_a$]	42.1	40.9	41.2	40.3	
[$K2_a$]	39.0	45.2	48.7	41.6	
[$K3_a$]	46.1	41.4	40.2	46.7	

It can be seen that sample 8 had the highest 90-day compressive strength for 51.0 MPa under the C3F2B1T3 test condition; the best combination was B2C3T3F2 from the range analysis graphs.The range test values in each column were used to measure the effects of the respective factors in the test. It can be seen through the above table that in the 90-day concrete compressive strength test, the factors that affected strength from strongest to weakest were carbonation time (B), water-cement ratio (C), freeze-thaw times (T), and fly ash content (F). Of these, the best combination was B2C3T3F2. Compared with the intuitive view angle (B1C3T3F2), the main difference was the carbonation time length (B). According to range analysis graphs, the carbonation time had the greatest influence on mortar strength. Select carbonation for 3 days as experimental factor, then the best combination B1C3T3F2 could be drawn, namely water-cement ratio of 0.50, content of fly ash of 20%, carbonation time of 3 days, and freeze-thaw times of 100 times.

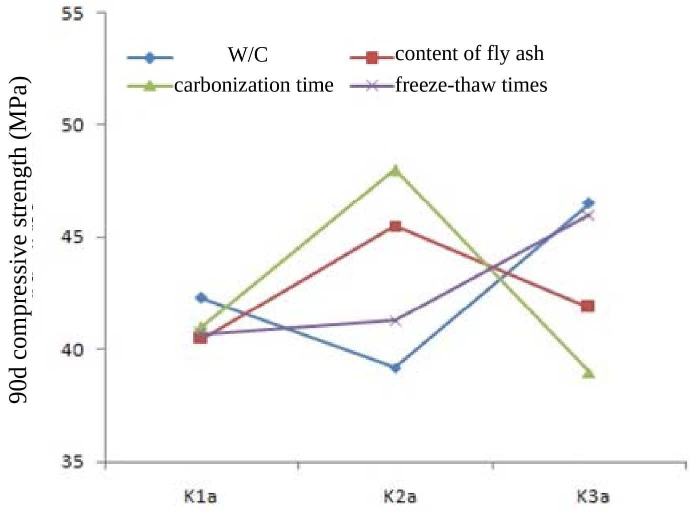

Figure 1. Range analysis curves (freeze-thaw after carbonation).

The reason why carbonation had a greater impact on mortar strength might be that during carbonation, solid material were made and became blocked inside of concrete pores, thus reducing the concrete's internal porosity; this weakened carbon dioxide diffusion that improved concrete density and strength. However, concrete alkalinity decreased after carbonation, and when the carbonation over the protective layer of concrete, it would make concrete lose protection for steel bar under conditions of water and air and the steel began to rust. The carbonation shrinkage cracks promoted rust expansion, which damage the protective layer of concrete; this created a self-perpetuating cycle that continuously degraded concrete strength.

As seen from the test results, the freeze-thaw cycle had the lowest impact on mortar intensity. One reason might be fewer freeze-thaw times which withstood freeze-thaw cycles of specimens, and the other was the generated calcium carbonate deposited in the pores of specimens during carbonation. After freeze-thaw cycle, the reduction in capillary pore volume meant a reduction in total expansion pressure for specimens. In addition, moisture migration became relatively difficult due to the compact structure, and the increase in seepage pressure correspondingly lagged behind, so concrete after carbonation could withstand more freeze-thaw cycles. However, it was not the case that longer carbonation times lead to better freezing resistance. The carbonation process was a precipitation process of calcium carbonate crystals, which lead to gradual contraction and crack formation. Therefore, carbonation improved the concrete's frost resistance to a certain extent. Under a certain time range, concrete freezing resistance would become stronger when carbonation time is longer.

Range analysis was also conducted for compressive strength results after freeze-thaw cycles and carbonation for 90 days. Figure 2 shows the water-cement ratio, fly ash content, carbonation times, freeze-thaw times, and impact on hydraulic concrete strength. Range analysis are shown is Table 7.

Table 7. Range analysis 2.

Specimen	C	F	T	B	Compressive strength in 90d (MPa)
S1	1	1	1	1	45.9
S2	1	2	2	2	39.7
S3	1	3	3	3	0
S4	2	1	2	3	53.9

S5	2	2	3	1	0
S6	2	3	1	2	38.2
S7	3	1	3	2	0
S8	3	2	1	3	41.4
S9	3	3	2	1	0
K1	85.6	99.8	125.5	45.9	
K2	92.1	81.1	93.6	77.9	
K3	41.4	38.2	0	95.3	
$K1_a$	28.5	33.3	41.8	15.3	
$K2_a$	30.7	27.0	31.2	26.0	
$K3_a$	13.8	12.7	0	31.8	

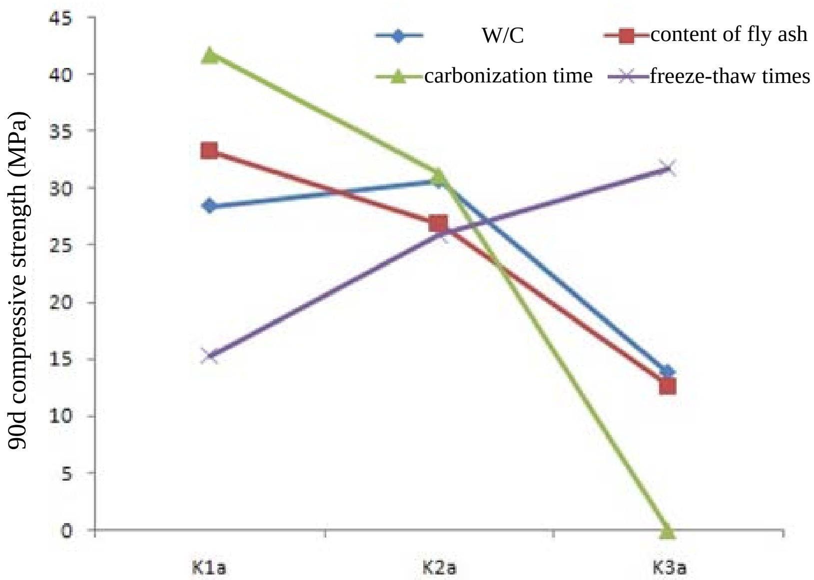

Figure 2. Range analysis curves (carbonation after freeze-thaw).

Sample S4 showed the highest 90-day compressive strength for 53.9 MPa under the C2F1B3T2 test condition; the best combination was B1F1T3C2 from the trend graphs. Range calculation showed that the factors affecting the 90-day compressive strength of concrete in order from greatest to weakest impact were carbonation time (B), fly ash content (F), freeze-thaw cycle times (T) and water-cement ratio (C). Compared with the intuitive view angle (B3F1T2C2), the main difference was the carbonation time length (T) and the freeze-thaw cycle time length. According to range analysis graphs, carbonation time had a greater influence on cement mortar compressive strength, followed by freeze-thaw time. Considering the test objectives and test results, choose carbonation for 14 days and freeze-thaw times of 100 times as experimental factors, then the best combination was with water-cement ratio of 0.45, none content of fly ash, carbonation time of 14 days, and freeze-thaw times of 50 times.

For specimens that suffered freeze-thaw cycles first, the carbonation time had the greatest impact on strength due to the expansion and osmotic pressures caused by water motion after thawing. This linked some of the original closed pores together, which loosened the specimen's internal organization and increased its total porosity. The longer the freeze-thaw time, the greater damage the specimen suffered, the greater the porosity was because carbon dioxide could quickly spread into the specimen. In addition, there were small cracks on the specimen's surface after the freeze-thaw cycle. Carbon dioxide entered the specimen through cracks, which made carbonation depth after freeze-thaw cycles much greater than those of specimens that had not endured freeze-thaw cycles. According to the mechanism of carbide, the carbonation generated calcium carbide; this and other solid materials clogged mortar pores, resulting in decreased porosity for the internal specimen, which ultimately improved mortar strength.

3.2. Dynamic elastic modulus

From the results in Table 8, for the specimen that endured carbonation after freeze-thaw cycle, the elastic modulus loss and loss rate gradually increased as the water-binder ratio increased when the fly ash content was 20%. When the specimen was carbonation only, the elastic modulus loss increased more than other specimen. Otherwise, the dynamic elastic modulus increased when the content of fly ash increased. When mixing with fly ash, the frost resistance of specimen became worse, but the dynamic elastic modulus increased.

Table 8. Relative dynamic elastic modulus of samples.

Specimen	W/C	FA(%)	Air content (%)	Relative dynamic elastic modulus	
				P_{50}	P_{100}
B1	0.35	0	4.5	97.41	96.04
B2	0.35	20	4.7	94.94	92.11
B3	0.45	20	5.0	92.08	89.26
B4	0.45	40	4.9	90.33	88.08
B5	0.55	20	4.8	89.96	86.43
B6	0.55	40	4.6	88.61	84.05
T1	0.35	0	4.5	96.06	93.99
T2	0.35	20	4.7	92.02	89.38
T3	0.45	20	5.0	90.09	85.87
T4	0.45	40	4.9	84.62	78.17
T5	0.55	20	4.8	83.43	80.30
T6	0.55	40	4.6	80.32	71.67

Under a certain condition, concrete frost resistance can improve after carbonation; solid materials were made during the carbonation process and deposited in specimen pores, which reduces porosity, and compact the structure. In the freeze-thaw process, the total swelling pressure is reduced, moisture migration is hindered, and the osmotic pressure increase correspondingly lags which lead to a improvement of frost resistance.

3.3. Flexural strength

(1) Table 9 shows the flexural strength of samples under the alternating action of freeze-thaw and carbonation. It can be seen that the flexural strength drop rate increases gradually, and, specimens conducted carbonation test followed by freeze-thaw test have larger flexural strength. When fly ash content was 20%, the specimen weight loss of the two groups increased as the water-binder ratio increased, and the loss rate also gradually increased.

(2) For specimens that endured carbonation test followed by a freeze-thaw test, the internal structure becomes dense, and the frost resistance was increased due to the filling effect of the calcium carbonate from carbonation. During the freeze-thaw process, the osmotic and swelling pressures of water can cause calcium carbonate to gradually decompose; in addition, some original closed pores begin indirect within one another, the internal tissues fluid becomes loose, and the compressive strength slightly declines than before. According to the previous measured dynamic elastic modulus, the frost resistance of the carbonized specimens was stronger than that of uncarbonized specimens

within a reasonable range of carbonation; as a result, the flexural strength was higher than that of specimens without carbonation.

(3) For specimens that endured a freeze-thaw test followed by a carbonation test, tiny cracks appeared on the specimen surface due to the osmotic and swelling pressures caused by water movement. This loosened the internal structure and increased total porosity.

Table 9. Flexural strength of samples under the alternating action of freeze-thaw and carbonation.

Samples	Gradation	W/C	Fly ash (%)	Air content (%)	Flexural strength(MPa)	
B1	Two	0.35	0	4.5	9.69	freeze-thaw followed by carbonation
B2	Two	0.35	20	4.7	8.19	
B3	Two	0.45	20	5.0	8.06	
B4	Two	0.45	40	4.9	6.56	
B5	Two	0.55	20	4.8	5.94	
B6	Two	0.55	40	4.6	5.31	
T1	Two	0.35	0	4.5	12.81	carbonation followed by freeze-thaw
T2	Two	0.35	20	4.7	11.25	
T3	Two	0.45	20	5.0	10.67	
T4	Two	0.45	40	4.9	9.69	
T5	Two	0.55	20	4.8	9.02	
T6	Two	0.55	40	4.6	5.94	

4. Conclusions

(1) For specimens that endured a freeze-thaw cycle first, the carbonation time had the greatest impact on strength due to the expansion and osmotic pressures caused by water motion. After thawing, some of the closed pores linked together, which loosened the internal organization and increased total porosity.

(2) When the fly ash content was constant, the dynamic elastic modulus loss, loss rate, and weight loss increased as the water-binder ratio gradually increased. The dynamic elastic modulus loss and weight loss of the carbonized specimens were smaller than those of uncarbonized specimens within a reasonable carbonation range. Specimens without fly ash content had the highest frost resistance, the lowest dynamic elastic modulus, and the lowest weight loss.

(3) For specimens that endured the carbonation test followed by a freeze-thaw test, and for specimens that endured a freeze-thaw test followed by carbonation test, the flexural strength declined as the water-binder ratio or fly ash content increased.

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