THE EFFECT ON CHLORIDE DIFFUSION FROM NON-STEADY-STATE ELECTRICALLY ACCELERATED METHODS USING DIFFERENT MIX PROPORTION AND CURING CONDITIONS

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Abstract

In Japan, the chloride diffusion coefficient generally has been using two different methods of experiment. However, these methods of calculation of the diffusion coefficient have some problems. For example, the immersion test requires to long testing time and the electrically accelerated test based on the steady state may differ from actual phenomenon. In this research, it focus on the electrical migration test based on the non-steady-state which can shorten the test time and is simple test. In order to comprehend effects of cement types, test duration and curing conditions on the diffusion coefficient, we used 7 types of cement and changed the test duration. Curing methods were Water, Seal and Dry. The penetration depth of the chloride ion by the non-steady-state method is substituted in equations by NT BUILD 492 of NORDTEST and the Public Works Research Institute (PWRI) in Japan for calculation the diffusion coefficient. As a result of calculating the diffusion coefficient by using the penetration depth at each test time, the difference between the diffusion coefficients by the each equation was small. However, the chloride diffusion coefficients at each the applied voltage durations weren't approximately the same value. And, the penetration depth was larger in the order of Dry-Seal-Water.

Keywords: electrical migration test based on the non-steady-state, chloride diffusion coefficient, applied voltage duration, cement types.

1. INTRODUCTION

There are several factors which cause deterioration of concrete structures. In particular, deterioration due to chloride damage is serious. It is important to predict the penetration of chloride ions in the concrete. The verification of salinity, penetration of chloride ion is predicted based on the diffusion Fick's law. In order to evaluate the limit state of steel corrosion, it is necessary to grasp the chloride ion diffusion coefficient. Methods of calculating the chloride ion diffusion coefficients are shown, in the Standard Specification for Concrete Structures of Japan. For example, it is calculation formula by function of water-cement ratio and accelerated test. The function of water-cement ratio has been determined to cement each type. However, this is based on the chloride ion concentration distribution survey obtained from actual structures and natural exposure specimen. Therefore, the function of water-cement ratio includes the impact of construction and environmental influences. In addition, cement types are limited. On the other hand, accelerated test is that of electrical migration test and immersion test. Feature of these tests is that it requires a long test period and that it must be a

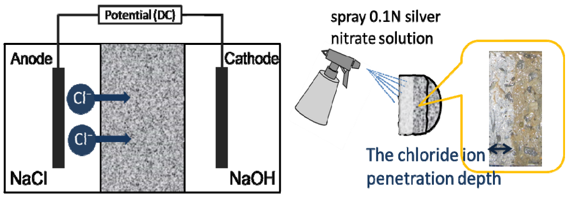


Fig. 1 Non-steady-state electrical migration test

chemical analysis to measure the chloride ion concentration. In addition, the chloride ion in the actual structures diffuses in the non-steady state. However, the traditional electrical migration test is a test in the steady state. This test is different from the inside of the actual structures. In NORDTEST, NT BUILD 492[1)] has been standardized as electrical migration test of non-steady-state. And in Japan, a method of calculating the diffusion coefficient by using the penetration depth of chloride ions in the non-steady state has been proposed[2)]. These tests are easier and shorter than the conventional method. The purpose of this research is to understand the influence on the diffusion coefficient by the applied voltage duration and cement-types. We calculated the diffusion coefficient from the formula of PWRI method and NT BUILD 492 by using the non-steady-state electrical migration test. Also, the diffusion coefficient of specimens which were cured by different methods was calculated from the non-steady-state electrical migration test.

2. EXPERIMENTAL OUTLINE

2.1 Non-steady-state electrical migration test

Fig.1 shows experimental equipment for non-steady-state electrical migration test. The pre-treatment was carried out saturating specimen in a vacuum with a calcium hydroxide solution. After the pre-treatment, 0.3N of NaOH was injected into anode side and 3% NaCl was injected into cathode side. After that, DC voltage of 30V was supplied for 3, 6, 12, 18, 24 and 36 hours. After the supply of each has been completed, the specimen was split in half and sprayed 0.1N silver nitrate solution on to the surface (Fig.1). In the split surface, the part which was colored in white was measured as the penetration depth of chloride ion. The penetration depth is the average value measured from the center to both edges at intervals of 10 mm.

2.2 Diffusion coefficient calculation methods

Chloride ion diffusion coefficients were calculated using NT BUILD 492 (1) and PWRI method equation (4). In NT BUILD 492, when using the N the chloride ion concentration Cd ≈ 0.07N of the white area, namely cement types are limited for apply to NT BUILD 492.In this study, the value of Cd was applied to other types of cement.

$$D_{nssm} = \frac{RT}{zFE} \cdot \frac{X_d - \alpha\sqrt{X_d}}{t} \qquad (1)$$

$$E = \frac{U-2}{L} \qquad (2)$$

$$\alpha = 2\sqrt{\frac{RT}{zFE}} \cdot erf^{-1}\left(1 - \frac{2C_d}{C_0}\right) \qquad (3)$$

Where, Dnssm: non-steady-state migration coefficient, m^2/s; z: absolute value of ion valence, for chloride, z = 1; F: Faraday constant, F = 9.648 ×104 J/(V·mol); U: absolute value of the applied voltage, V; R: gas constant, R = 8.314 J/(K·mol); T: average value of the initial and final temperatures in the analyte solution, K; L: thickness of the specimen, m; xd: average value of the penetration depths, m; t: test duration, seconds; erf^{-1}: inverse of error function; Cd: chloride concentration at which the colour changes, Cd ≈ 0.07 N for OPC concrete; C0: chloride concentration in the catholyte solution, C0 ≈ 2 N.

$$D = k \cdot \frac{RT}{zF} \cdot \frac{L}{\Delta\emptyset} \qquad (4)$$

Where, D: Diffusion coefficient, m^2/s; k: ratio of penetration depth on chloride ion, m/s, Δφ; absolute value of the applied voltage, V

3. VIABILITY OF THE APPLICATION OF NON-STEADY-STATE ELECTRICAL MIGRATION TEST

3.1 Specimen outline

It has to prepare 7 types cement such as ordinary Portland cement(N), high-early-strength Portland cement(H), Low heat Portland cement (L), blast furnace slag cement type A(BA), blast furnace slag cement type B(BB), blast furnace

Table 1 Mix proportion-1

Cement Type	W/C (%)	s/a (%)	Unit weight(kg/m³) W	C	BFS	FA	S	G	SL (cm)	Air (%)
N				313	-	-	869	968	14.5	5.8
H				313	-	-	869	967	14.5	4.5
L		48		313	-	-	872	971	14	6
BA	55		172	219	94	-	866	963	9.0	4.3
BB				188	125	-	868	965	13.0	3.7
BC		50		92	219	-	903	927	10.0	3.6
FB				250	-	63	896	919	16.5	4.0

slag cement type C(BC) and fly ash cement type B (FB). Blast furnace slag cement and fly ash cement were replace cementwith blast furnace slag and fly ash. Flesh concrete were casted for molds (φ100×200mm), and those specimens were demold the next day. After 28 days of water-curing, specimens of 100mm in the central portion is cut in two. These were used as specimens.

3.2 Chloride ion penetration depth

Figure 2 shows the relationship between the penetration depth and the applied voltage duration. Regardless of cement type, as the penetration depth increased application time becomes longer. The penetration depth of the same the applied voltage duration is larger in the order of L, FB, N, H, BA, BB, and BC. H and N had a similar penetration depth at any the applied voltage duration. The penetration depth of L and FB were not measured for the specimen supplied for 36 hours. Because the entire split surface of L and FB had already colored to white before this 36 hours. In other cement, white area did not reach up to 50mm in the supply for 36 hours.

3.3 Comparison of diffusion coefficient

3.3.1 Effect of calculation methods

Figure 3 shows a comparison of the diffusion coefficient by calculation formulas. The diffusion coefficients were calculated using the penetration depth obtained from the results of applying voltage for 24 hours to equation (1) and the rate of penetration of 3 to 24 hours to equation (4). The result of comparing diffusion coefficient shows that difference in the diffusion coefficient by each calculation formula is small

Fig. 2 Penetration depth of chloride ion

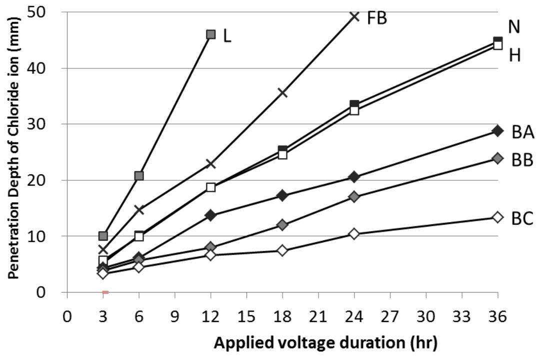
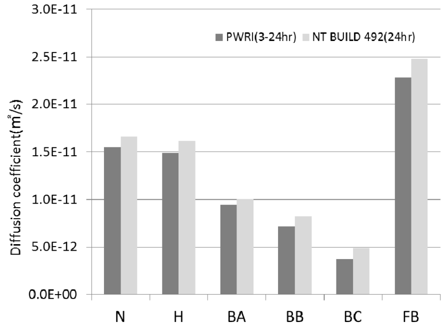


Fig. 3 Diffusion coefficient of each cement



types

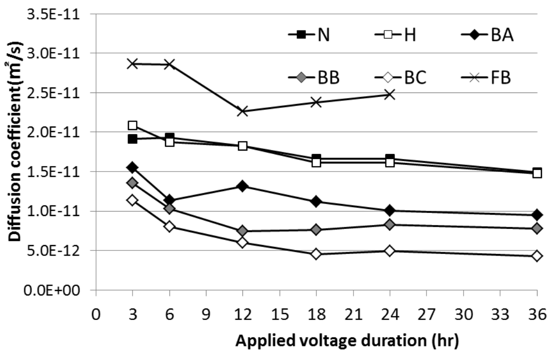


Fig. 4 Diffusion coefficient on each the applied voltage duration

regardless of the cement types. Therefore, there is not much difference in the diffusion coefficient of NT BUILD 492 and PWRI method.

3.3.2 Effect of cement types

The diffusion coefficient of the cement types other than N is calculated using Cd ≈ 0.07N which was limited only to N in NT BUILD 492. Figure 3 shows the compare of diffusion coefficient to cement each type. All the cement types, the difference between the diffusion coefficient of NT BUILD 492 and PWRI is small. For N and BB, this difference was

Table 2 Mix proportion-2

Cement Type	W/C (%)	s/a (%)	Unit weight (kg/m^3)					SL (cm)	Air (%)
			W	C	BFS	S	G		
N	30	50	165	550		804	838	8.5	4.5
	60		175	292		897	935	9.5	4.8
BB	30		165	275	275	794	828	12	3.8
	60		175	146	146	892	930	11	4.9

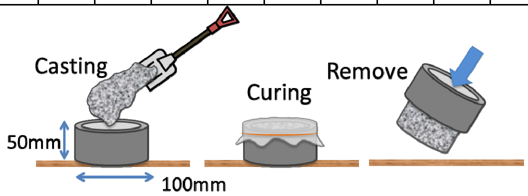


Fig. 5 specimen for examination of curing

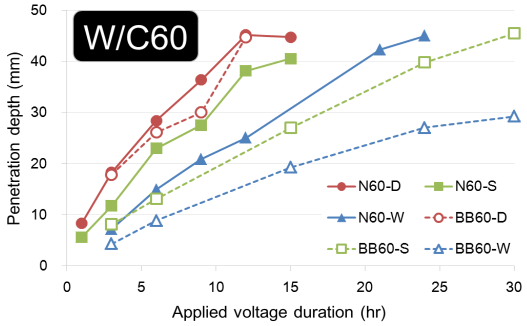


Fig. 6 Penetration depth (W/C 60%)

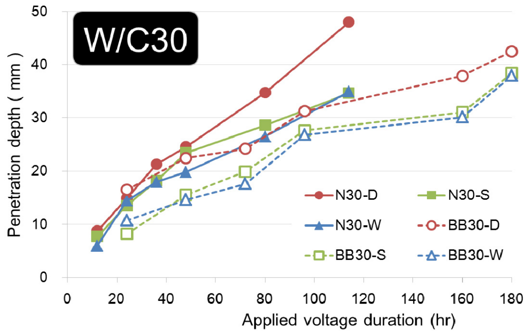


Fig. 7 Penetration depth (W/C 30%)

specially small. Accordingly, NT BUILD 492 might be supplied to each cement types other than N.

3.3.3 Effect of the applied voltage duration

Figure 4 shows the diffusion coefficients were calculated using the NT BUILD 492 and the penetration depth obtained changing applied voltage duration. The diffusion coefficient of the FB was calculated for 24 hours the applied voltage duration. In any cement, diffusion coefficient becomes smaller as the conduction time is prolonged until 18 hour the applied voltage duration. Then, the diffusion coefficient

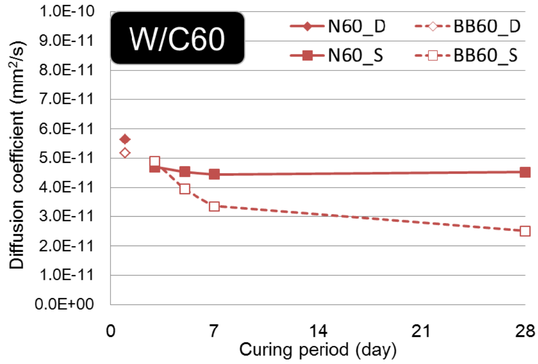


Fig. 8 Relationship of the diffusion coefficient and curing period (W/C 60%)

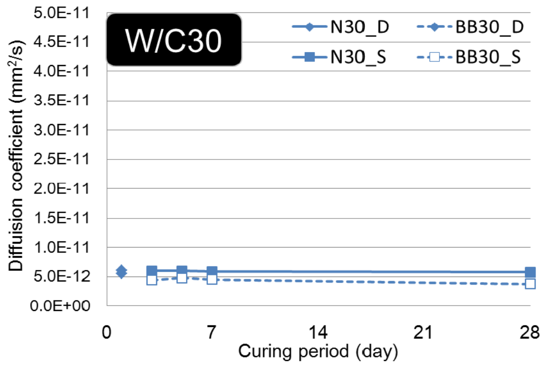


Fig. 9 Relationship of the diffusion coefficient and curing period (W/C 30%)

became generally flat. Further, as also shown in Figure 2, the penetration depth tends to increase with the lapse of the energizing time. On the other hand, the diffusion coefficient calculated from the depth of penetration was reduced as the power-on time becomes longer. It is necessary to clarify why the chloride diffusion coefficient decreases regardless of applying voltage.

4. VARIATION ON THE CURING CONDITIONS

4.1 Specimen outline

It has to prepare two types cement such as ordinary Portland cement(N) and blast furnace slag cement type B(BB). Water-cement ratio was 30% and 60%. This is because effects of the curing period and curing method are to come out remarkably. It was conducted a research showing that concrete is susceptible to dry to a depth of 30 mm from the surface [3]. Therefore, it can't be dried uniformly in specimens such as 3.1. (φ100 × 50mm). In this study, specimens were made using the mold of PVC pipe in consideration of curing conditions (Figure 5). The shape of specimen is a disk-shaped (φ100 × 50mm). Curing method were water(W), seal(S28) and dry(D1) . Seal curing period were 3(S3), 5(S5), 7(S7) and 28(S28). After curing, specimens that have been removed from the mold were left at a temperature-controlled room until 28 days.

4.2 Effects of curing conditions

4.2.1 Chloride ion penetration depth

Figure6 and 7 show the relationship between the applied voltage duration and the penetration depth in different curing conditions. The penetration depth of water cement-ratio 60% was larger in the order of D, S and W. But, as a result of water-cement ratio 30%, there is no difference in penetration depth of W and S. There is a report that in case of water-cement ratio is low, the penetration depth of water curing and seal curing are about the same[4]. This reason is that it is possible that hydration degree is the same in the water curing and seal curing. Compared to N, the penetration depth of BB was small in the case of W and S. Because, it is considered that BB becomes denser than N with the progress of hydration and has the higher ability to immobilize chloride ion. In the case of W/C 60%, there was no difference in the penetration depth of N and BB which was dry cured.

4.2.2 Curing period and diffusion coefficient

Figure 8 and 9 show the diffusion coefficient of 60% water-cement ratio which was calculated using the penetration depth when applied voltage for 48 hours. The diffusion coefficient was decreased as the curing period is longer. Diffusion coefficients of specimens which were cured for more than 6 days were same value. The diffusion coefficient of W/C 30% was not significantly affected by the curing period. Consequently, BB is susceptible to the influence of curing. And, BB which was cured carefully, have the chloride ion resistance improved.

CONCLUSIONS

The results of this research are summarized as follows:

(1) For each cement type, the diffusion coefficients calculated using the NT BUILD 492 and the PWRI method were found to be similar.

(2) For each cement types, as the applied voltage duration becomes longer the penetration depth increased. However, the diffusion coefficient became smaller, then the diffusion coefficient became generally flat.

(3) Water cement-ratio 60%, the penetration depth was larger in the order of Dry- Seal-Water.

(4) The diffusion coefficient was decreased as the curing period is longer. It becomes clear that BB is susceptible to curing.

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