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Experimental Study on the Time-dependent Property of Chloride Diffusivity

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ABSTRACT

Estimation method of chloride diffusivity by concentration difference is time-consuming. In recently study, therefore, chloride diffusivity of concrete is mainly conducted by electrically accelerated method, which is accelerating the movement of chloride ion by potential difference. In this study, Portland cement concrete and 2 types of concrete containing with ground granulated blast-furnace slag (40% and 60% wt. of cement by weight) with four steps of water-cement ratio were manufactured. To compare with chloride diffusivity calculated from the electrically accelerated test and immersed test in artificial seawater, chloride diffusivity tests were conducted. From the results of regression analysis, regression equation between accelerated chloride diffusivity and immersed chloride diffusivity was linear function. And the determinant coefficient was 0.96 for linear equation. So it is possible that we can predict the immersed chloride diffusivity with 95% confidence interval.

INTRODUCTION

The chloride diffusivity of concrete is an important index in planning the durability and in selecting the reinforced material as well as an important material to predict an initial time of corroding reinforced structures.

On the other hand, In Korea, when the designing life of concrete structures is a first grade, more than 100 years is required. It, therefore, is not easy to predict results of over 10 years or 100 years from the test result at a relatively initial age. Accordingly, it is important to grasp a time-dependent property of chloride diffusivity which is a main variance to predict the initial time of corroding a reinforced material.

The penetration and diffusion of ions in ocean environments are frequently regarded as the diffusion by a concentration difference, which becomes a diffusion condition of non-steady state. Therefore, the chloride diffusivity of concretes is, usually, experimentally obtained by the diffusion due to a concentration difference, but many efforts and times are required. Regarding the time-dependent property of the diffusivity due to such field condition or immersion test, numerous researches have been proceeded. But the research results on time-dependent property of chloride diffusivity due to electrically accelerated test are a few. Accordingly, considering that the chloride diffusivity of concretes is time-dependent, this study has experimentally evaluated six accelerated chloride diffusivity-dependent properties measured at ages up to 730 days for concrete specimen prepared by four steps of water-cement ratio and two steps of ground granulated blast furnace. Also, this study has analyzed the correlation between the accelerated chloride diffusivity at each age, and appearance diffusivity immersed and obtained in two times concentration of artificial seawater.

EXPERIMENTS PROCEDURE

Materials and mix proportions of concrete. Three kinds of binders where ground granulated blast-furnace slag (GGBFS) is mixed at cement weight ratio 0% (NPC), 40% (S4C) and 60% (S6C) with ordinary Portland cement (OPC), were used in the experiments. The chemical composition and physical properties of the cement and mineral admixture are shown in Table 1.

Table 1. Chemical Composition and Physical Properties of Cement and GGBFS

	Chemical compositions (%)							Physical properties	
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Ig. loss	Density(g/cm^3)	Blaine(cm^2/g)
OPC	19.88	4.87	3.11	61.56	2.95	2.82	0.78	3.15	3,120
GGBFS	31.88	12.64	0.39	42.46	6.38	3.63	0.65	2.92	4,450

River sand was used as fine aggregate and crushed stone with maximum size of 25*mm* was used as coarse aggregate for production of all concretes. The physical properties of the aggregates are listed in Table 2.

Table 2. Physical Properties of Aggregates

	G_{max}(mm)	Density(g/㎤)	Absorption(%)	Unit weight(kg/㎥)	F.M.
Fine aggregate	-	2.59	0.80	1,581	2.65
Coarse aggregate	25	2.62	0.78	1,533	6.83

Mixture proportions of concrete have been determined with 40%, 45%, 50% and 60% water-cement ratio (*W/cm*) for three types of cement. GGBFS were mixed in 40% and 60% with respect to a weight of cement. Table 3 summarizes the mix proportions of total 12 combined concretes.

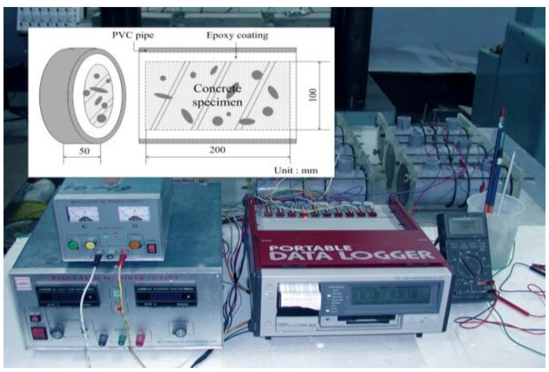
Table 3. Mixture Proportions of Concrete

	G_{max} (mm)	Slump (cm)	Air (%)	W/cm (%)	S/a (%)	Unit weight (kg/㎥)				
						W	C	S	G	GGBFS
NPC40	25	15±2	4.5±1.0	40	41	187	467	655	958	-
NPC45	25	15±2	4.5±1.0	45	42	187	416	689	967	-

NPC50	25	15±2	4.5±1.0	50	43	187	374	720	970	-
NPC60	25	15±2	4.5±1.0	60	45	187	312	777	964	-
S4C40	25	15±2	4.5±1.0	40	41	187	280	651	951	187
S4C45	25	15±2	4.5±1.0	45	42	187	250	685	960	166
S4C50	25	15±2	4.5±1.0	50	43	187	224	716	964	150
S4C60	25	15±2	4.5±1.0	60	45	187	187	773	960	125
S6C40	25	15±2	4.5±1.0	40	41	187	187	648	947	280
S6C45	25	15±2	4.5±1.0	45	42	187	166	683	957	250
S6C50	25	15±2	4.5±1.0	50	43	187	150	714	961	224
S6C60	25	15±2	4.5±1.0	60	45	187	125	771	957	187

Electrically accelerated test. To obtain an electrically accelerated chloride diffusivity, the curing was carried out in water for ages of 28, 56, 120, 180, 365 and 730 days, and concrete specimen was coated with epoxy and cut at thickness of 50mm to a diffusion cell as shown in Fig. 1 (Moon et al., 2003).

Fig. 1. Experimental Device of Accelerated Test by Potential Difference



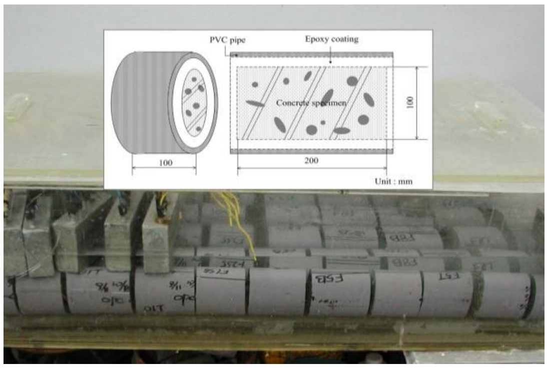
The test specimen was applied to a potential difference of 600*V/m* for eight hours, and movement of chloride ion was accelerated. The concrete specimens were split axially using a standard universal testing machine and sprayed with 0.1N $AgNO_3$. The accelerated chloride diffusivity (D_{acc}) was obtained using the following Eq. 1 from an average chloride penetration depth measured at 20 places with an interval of 5*mm* for the splitting surface (Tang et al. 1993). As the electrolyte, 0.5*M* sodium chloride and saturated calcium hydroxide were used for a cathode cell, and a saturated calcium hydroxide was used for an anode cell.

$$D_{acc} = \frac{R \cdot T \cdot L}{z \cdot F \cdot U} \cdot \frac{x_d - \alpha\sqrt{x_d}}{t} \qquad \text{(Eq. 1)}$$

Where, D_{acc} : accelerated chloride diffusivity (m^2/s), R : gas constant, T : absolute temperature, L : specimen thickness (m), z : ion electrovalence, F : Faraday`s constant, U : potential difference (V), x_d : chloride penetration depth (m), α : experiment constant (23,600m^{-1}), t : applied time (s)

Immersion test of artificial seawater. Concrete specimens were cured in water for age of 28 days, coated with epoxy, cut with 100*mm* and immersed in artificial seawater with two times concentration for 180 days as shown in Fig. 2. The artificial seawater was prepared by ASTM D 1141 "Standard Specification for Substitute Ocean Water.

Fig. 2. Experimental Device of Immersion Test by Artificial Seawater



The powder sample of concrete was prepared at dry furnace at 105^{o}C after extracting a powder from the surface of specimen, to thereby measure an acid-soluble chloride weight. The total chloride content in concrete was directly titrated out using a combination electrode and a standard solution (0.1N $AgNO_3$ solution), and calculated from Eq. 2(AASHTO T 260).

$$Cl^{-}(\%) = 3.5453 \times \frac{N \cdot V}{W} \qquad \text{(Eq. 2)}$$

Where Cl^{-} : normality of chloride ion (%), N : normality of $AgNO_3$, V : $AgNO_3$ volume (*ml*), W : weight (*g*)

On the other hand, when the diffusion of ion in concrete is non-steady state, it can be applied to Fick`s second law like Eq. 3.

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} \qquad \text{(Eq. 3)}$$

Where $C(x, t)$: concentration of ion, D : diffusion coefficient of ion, t : time, x : distance

In the below initial condition and boundary condition, an analytic solution of Fick`s second law is given in Eq. 4.
- Initial condition : $C(x, 0) = C_i$, for t =0
- Boundary condition : $C(0, t)=C_s$, for x = 0

$$C(x,t) = C_i + (C_s - C_i) \cdot erfc\left(\frac{x}{\sqrt{4D \cdot t}}\right) \qquad \text{(Eq. 4)}$$

According to Abramowitz et al.(1970), the complementary error function of Eq. 4 can be represented in approximate equation like Eq. 5.

$$erfc(x) \approx \left(1 - \frac{x}{\sqrt{3}}\right)^2, \quad 0 \le x \le \sqrt{3} \qquad \text{(Eq. 5)}$$

Substitution of Eq. 5 with Eq. 4 is as shown in Eq. 6.

$$\sqrt{C(x,t) - C_i} = -\sqrt{\frac{C_s - C_i}{12D \cdot t}} + \sqrt{C_s - C_i} \qquad \text{(Eq. 6)}$$

Eq. 6 has a pattern of $y = \alpha \cdot x + \beta$, the chloride amount per depth is analyzed by a linear regression to give α and β. The chloride diffusivity (D_{pond}) can be obtained by using Eq. 7.

$$D_{pond} = \left(\frac{\beta}{\alpha}\right)^2 \cdot \frac{1}{12t} \qquad \text{(Eq. 7)}$$

RESULTS AND CONSIDERATION

Penetration depth of chloride ion. The penetration depth of chloride ion is summarized by a kind of binder, an age and W/cm and shown in Fig. 3.

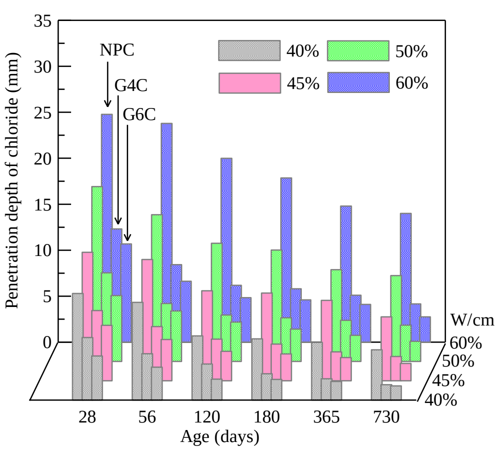


Fig. 3. Penetration Depth of Chloride Ion by Accelerated Test

From this figure, it can be seen that the penetration depth of chloride ion is high as a W/cm is increased, but it has a tendency to decrease as a replacement ratio of GGBFS and age are increased. The chloride penetration depths of Portland cement concrete (NPC) with same W/cm and GGBFS concrete are a little different according to ages, but when compared with

NPC concrete, it can see that there are reduction effects, a GGBFS 40% and 60%-combined concrete (S4C, S6C) reduce to 53% and 65% at age of 28 days, and to 83% and 90% at age of 730 days, respectively.

Such result conforms to the study result by Leng et al. (2000) that the chloride penetration depth of GGBFS concrete is greatly reduced because a potential hydraulic property of GGBFS is increased according to an increase of an age. And the addition of mineral admixtures like GGBFS can modify the microstructure of cement matrix by forming more C-S-H gel from latent hydraulic reactions and by filling the pores with their fine particles (Shiqun. et al., 1986). Thus, low permeability of cement matrix with GGBFS limits the penetration of aggressive ions such as chloride ion, sulfate and carbon dioxide.

Chloride diffusivity by accelerated test. To evaluate the chloride diffusion properties of concretes at ages up to 730 days, the chloride diffusivity calculated from the chloride penetration depth is summarized by kinds of concretes and shown in Fig. 4.

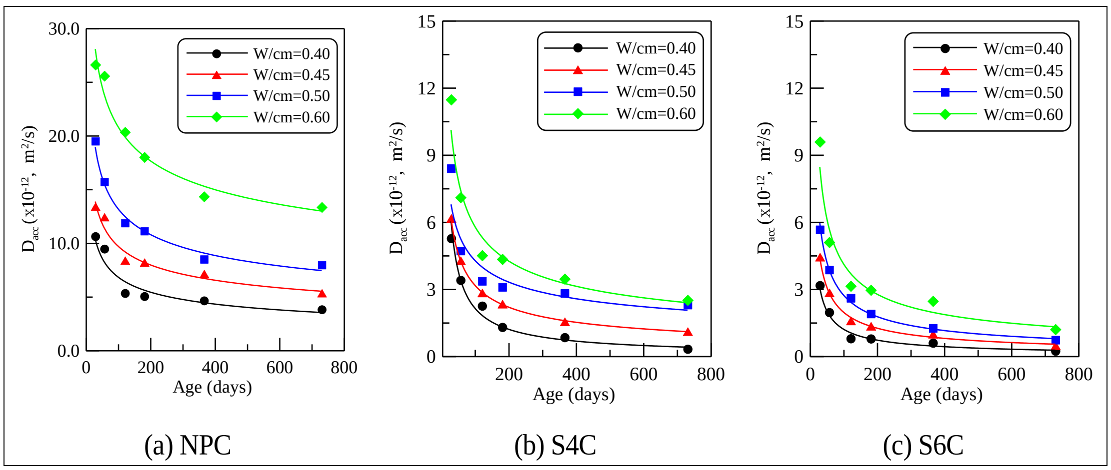


Fig. 4. Chloride Diffusivity by Accelerated Test

From this Figure, it can be seen that the chloride diffusivity was greatly different according to concrete W/cm and replacement ratio of GGBFS, and were reduced in power function according to an increase of ages. The chloride diffusivity at age (730 days) of NPC concrete was uniformly reduced irrespective of W/cm as compared with age of 28 days. However, it could be seen that the chloride diffusivity of GGBFS concrete was converged as age is increased and as a replacement ratio of GGBFS is increased irrespective of W/cm.

The chloride diffusivity measured at age of 28 days are 10~26x10^{-12}(m^2/s) according to W/cm for NPC concrete, 4~11x10^{-12}(m^2/s) at 40% replacement for GGBFS concrete, and 3~10x10^{-12}(m^2/s) at 60%. As compared with NPC concrete, there were reduction effects of average 55% and 68%, respectively. Also, it can be seen that the chloride diffusivity of

GGBFS concrete at age of 365 days were greatly reduced to average 20% and 10% of the diffusivity of NPC concrete at replacement ratio of 40% and 60%.

The time-dependent property of chloride ion conforms to the study result of Mangat et al.(1994) and Tumidajski et al.(1995). The reason is that the hydrated structure of concrete is dense according to an increase of age, a connectivity of porosity is reduced and flexibility is increased to thereby inhibit the penetration and diffusion of chloride ion.

On the other hand, the study result of time-dependent property of chloride diffusion coefficient due to field exposure test or immersion test is summarized and shown in Table 4 and Fig. 5.

Table 4. Pattern of Function Showing Time Dependent Property

Type of Equation	Remark
$D(t) = \alpha \cdot t^{-\beta}$	Type I
$D(t) = \xi + (1-\xi) \cdot \sqrt{28/t}$ *or* $D(t) = \alpha + \beta / \sqrt{t}$	Type II

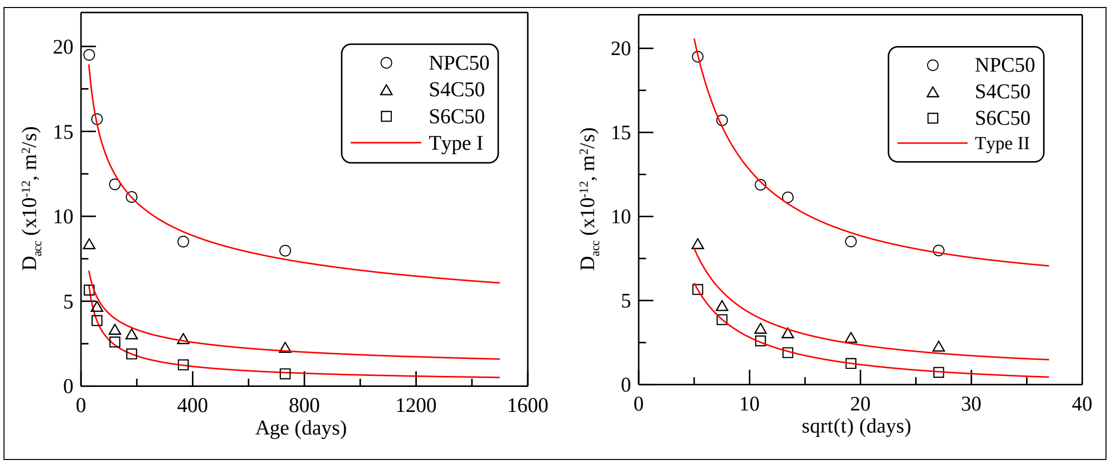


Fig. 5. Time-dependent Property of Chloride Diffusivity of Accelerated test

The pattern of function showing the time-dependent property of the diffusion coefficient of chloride ion by a potential difference at W/cm=0.50 is summarized and shown Table 5.

Table 5. Regression Analysis Result and Coefficient of Determination

	NPC50			S4C50			S6C50		
	α	β	R^2	α	β	R^2	α	β	R^2
Type I	49.077	0.2856	0.98	22.894	0.3642	0.89	46.413	0.6154	0.99
Type II	4.9484	78.203	0.99	0.4455	38.297	0.92	-0.4296	32.3986	0.99

In the case of Type II, because the diffusion coefficient of chloride ion due to characteristic of function is reduced without limitation according to an increase of age, this study analyzed the time dependent property of diffusion coefficient of chloride ion by Type I.
Accordingly, the time dependent property by concrete combination is summarized by Eq. 8, a pattern of power function, and shown in Table 6.

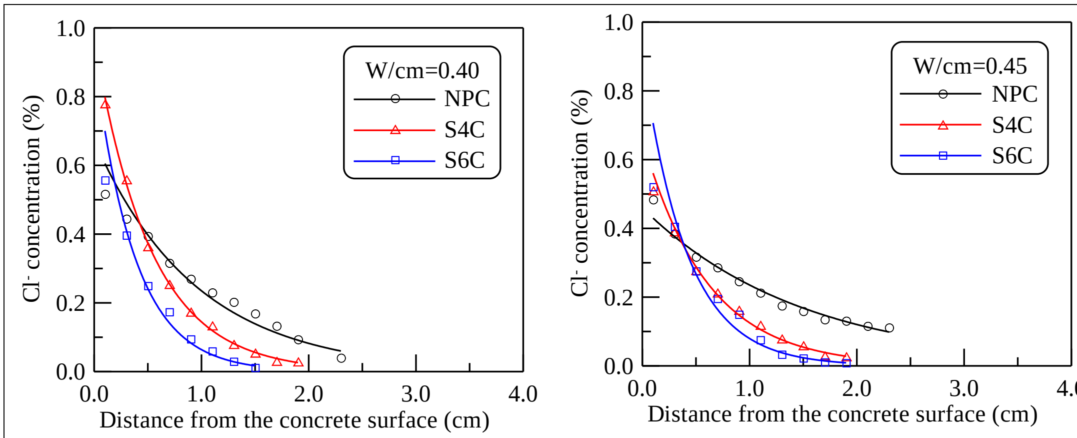
$$D_{acc}(t) = \alpha \cdot t^{-\beta} \times D_{28} \qquad \text{(Eq. 8)}$$

Where $D_{acc}(t)$: chloride diffusivity after time t (day), D_{28} : chloride diffusivity measured at age of 28 days, and α and β : experimental constant

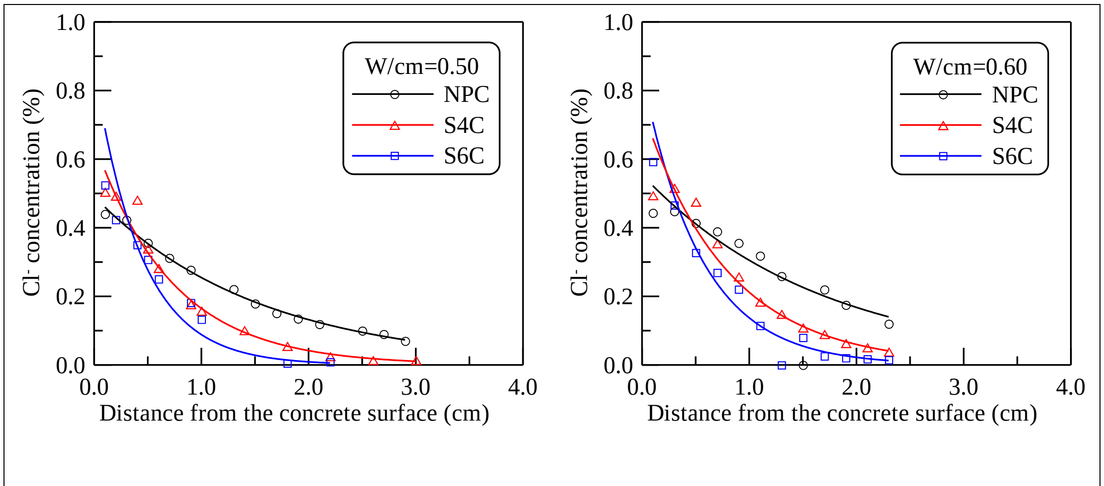
Table 6. Time Dependent Property Parameter by Concrete Combination

	NPC				S4C				S6C			
	40	45	50	60	40	45	50	60	40	45	50	60
D_{28}	10.66	13.45	19.53	26.65	5.29	6.19	8.42	11.49	3.19	4.46	5.68	9.61
α	2.90	2.64	2.51	2.32	1.56	5.73	2.72	3.83	10.96	8.35	8.17	5.84
β	0.33	0.28	0.29	0.24	0.82	0.52	0.63	0.44	0.73	0.64	0.62	0.57
R^2	0.91	0.96	0.98	0.97	0.97	1.00	0.89	0.96	0.96	0.98	0.99	0.95

Concentration profile from immersion test. To compare the chloride diffusivity (D_{acc}) of electrically accelerated test with chloride diffusivity (D_{pond}) obtained from the immersion test, the immersion tests of artificial seawater with two times concentration are conducted. Fig. 6 shows chloride profile by depth of concretes according to W/cm.



(a) W/cm=0.40 (b) W/cm=0.45



(c) W/cm=0.50 (d) W/cm=0.60

Fig. 6. Chloride Profile by Depth of Concrete

It can be seen that chloride concentration profile of NPC concretes is greatly different from GGBFS concretes. For GGBFS concrete, it can be seen that chloride ion is fixed and concentrated on the concrete surface and thereby the chloride concentration is greatly reduced according to a distance from the surface as compared with NPC concrete. The reason is that GGBFS concrete has a more content of C_3A than NPC concrete, and many chloride ions are chemically bound to form Friedel's salt ($C_3A \cdot CaCl_2 \cdot 10H_2O$). This confirms a result similar to the study of Buenfeld et al.(1990).

Chloride diffusivity by concentration profile. Chloride diffusivity obtained from chloride ion profile is summarized by kinds of concretes and W/cm and shown in Fig. 7.

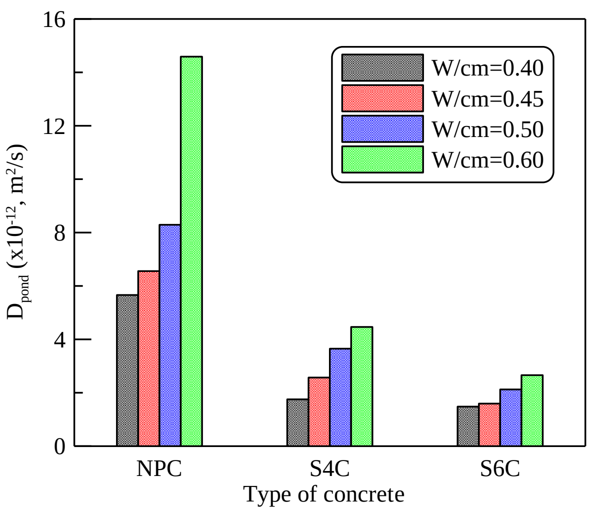


Fig. 7. Chloride Diffusivity by Immersion Test

Chloride diffusivity of NPC concrete is increased according to an increase of W/cm, but that of GGBFS concrete is almost similar irrespective of W/cm as a replacement ratio of GGBFS is increased. We think that cement hydrated product by a latent hydraulic reaction of GGBFS is reacted with $Al_2O_3^{2-}$, SiO^{2-} and the like, and the resulting C-S-H, C-A-H and AFm phase are filled with a large porosity between hydrated products of Portland cements to reduce the pore connectivity and increase the tortuosity of capillary pore in concrete.

Comparison of D_{acc} and D_{pond}. Chloride diffusivity by an accelerated test (D_{acc}) is wholly higher than chloride diffusivity by an immersion test (D_{pond}). The result of the linear regression analysis between them is summarized in Fig. 8.

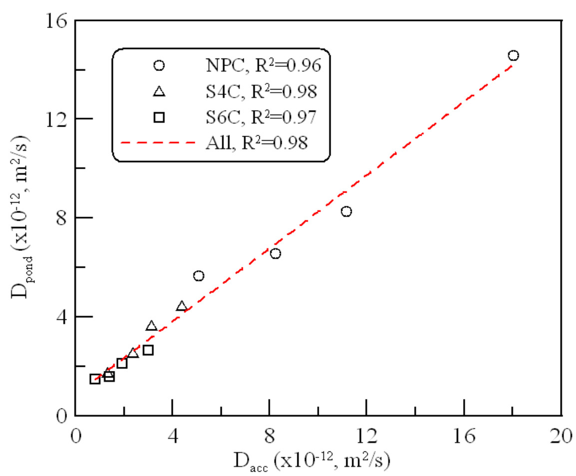


Fig. 8. Relationship Between D_{acc} and D_{pond}

The result of regression analysis shows that the coefficient of determination is more than 0.96 irrespective of kind of concrete, and there is a good correlation between the chloride diffusivity obtained from accelerated and immersed tests. It can be seen that it is possible to predict the chloride diffusivity from the result of electrically accelerated test with a high reliability.

CONCLUSION

In concretes obtained in this study step, the results of comparison and analysis of the chloride diffusivity obtained from accelerated and immersed tests are as follows.

- The penetration depths of Portland cement with the same water-cement ratio and GGBFS are a little different according to ages, but as compared with NPC concrete, in the case of age of

28 days, GGBFS to 40% and 60% combined concretes were reduced to 53% and 65%. In the case of age of 731 days, they were reduced to 53% and 65%, respectively.

- Chloride diffusivity obtained from the penetration depth of chloride ion has a tendency to reduce according to a lapse of age, GGBFS concrete permeability is greatly reduced as compared with NPC concrete permeability. Also, the chloride diffusivity of GGBFS concrete has a tendency to concentrate on one spot according to an increase of age.
- The concentration difference of chloride ion by depth shows a large difference according to the difference of the binding capacity of chloride ion according to the kind of binder. In the case of GGBFS concretes, the chloride diffusivity is relatively lower than NPC concrete as the chloride ion is bound within about 10*mm* from the surface.
- From the result of the chloride diffusivity obtained from accelerated and immersed tests, the regression equation of linear function pattern can be obtained. The coefficient of determination is more than 0.96 and has a good correlation irrespective of kind of concrete. That is, the reliability is more than 95%. The chloride diffusivity can be predicted from the result of electrically accelerated test.

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