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Effect of the Pore Structure of Concrete on the Compressive Strength of Concrete and Chloride Ions Diffusivity into the Concrete

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Abstract

The transport characteristics of deleterious ions such as chlorides depend on the pore structures of concrete and are the major factors in the durability of concrete structures in subjected to chloride attack such as in marine environments. In this paper, the effect of the pore structure on compressive strength and chloride diffusivity of concrete was investigated. Six types of concretes were tested.

The pore volume of concrete containing mineral admixtures increased in the range of 3 ~ 30nm due to micro filling effect of hydrates of the mineral admixtures. There was a good correlation between the median pore diameter, the pore volume above 50nm and compressive strength of concrete, but there was not a significant correlation between the total pore volume and compressive strength. The relationship between compressive strength and chloride diffusivity were not well correlated, however, pore volume above 50nm were closely related to the chloride diffusion coefficient.

***Keywords:** chloride ion, diffusion coefficient, pore size distribution, median pore diameter, total pore volume, compressive strength, mineral admixture*

1. Introduction

Chloride ions penetrate into concrete by various transport mechanisms such as diffusion and permeation due to concentration and pressure gradients, and adsorption due to capillary surface tension. The transport characteristics of chloride ions influence the initiation time and the rate of steel corrosion in concrete. Therefore, the penetration of chloride ions into concrete is considered as a major factor in determining the service life of concrete structures in chloride environments.[1~3)]

It is well known that the micro-pore structure of concrete depends on the degree of hydration, type of cement and binders, and mixture proportions. Making a dense concrete improves the strength and enhances the durability of concrete. It has been reported that mineral admixtures such as fly ash, ground granulated blast furnace slag and silica fume refine the pore size and its distribution and, accordingly, influence the strength and durability of concrete. Mineral admixtures react with cement hydrates forming dense micro-structures in the cement matrix, which hinders the penetration of deleterious substances into concrete.[4~6)]

Because of these effects, it is recommended that mineral admixtures be used for the construction of durable concrete structures in marine environments. In Japan, blended cement containing ground granulated blast furnace slag is generally used in marine environments.[7~9)] In Korea, however, sulfate resistant Portland cement or epoxy-coated reinforcement has generally been used in concrete structures as a counter measurement against chloride attack in the marine environment. Blended cement containing mineral admixtures had rarely been used in Korea until the Korean concrete standard specifications were revised in 1999.[10~12)] The main reason why blended cement containing mineral admixtures was not used in Korea was the quality variance of the domestic mineral admixtures, requirement of high development of strength in fields and uncertain understanding of effect of mineral admixtures on durability.

Therefore, in this paper, concretes containing 6 types of

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cements were studied, and the relationship between pore size distribution, compressive strength and chloride diffusivity was investigated. These results give fundamental data for verifying the control mechanism of chloride penetration and are helpful in selecting the proper cementitious materials for marine environments.

2. Experimental program

2.1. Materials

(1) Cements

Six types of cements were used in this study : OPC(Ordinary Portland Cement, Type I), LHPC(Low Heat Portland Cement, Type IV), SRPC(Sulfate Resistance Portland Cement, Type V), TBC(Ternary Blended Cement consists of OPC, fly ash and ground granulated blast furnace slag(GGBF) by specific percentages), Slag 40(OPC 40 % + GGBF 60 %) and Slag 60(OPC 60 % + GGBF 40 %).

OPC, LHPC and SRPC satisfy the KS L 5201. GGBF was used as a mineral admixture. The chemical composition and physical properties of OPC, LHPC, SRPC and TBC and the mineral admixture are listed in Table 1.

(2) Aggregate

Beach sand, which was washed out to be free chlorides, was used as the fine aggregate. The specific gravity and fineness modulus of the sand were 2.61 and 2.89, respectively. Crushed stone with maximum size 20 mm and a specific gravity 2.61 was used as the coarse aggregate.

2.2. Testing methods

(1) Measurement of porosity and pore size distribution

After water curing for 1 month, the concrete specimens were crushed and mortar pieces were obtained. The pieces weighed about 1.5g and were kept in a dry oven at 105～110℃ for 24 hours.

The mercury intrusion porosimetry (MIP) technique was employed with a contact angle 130.0 degree and a maximum pressure of 4,200kgf/cm^2 for the investigation of pore volume and structures in the range of 3～3.6x10^5 nm diameter.

(2) Test set-up for chloride diffusivity by electrical

Fig. 1 shows the test set-up for the measurement of chloride diffusivity. This set-up was developed by Dhir.[13] The cathode electrode is connected to the stainless steel plate(ANSI 316) in 0.5 mol/*l* chloride solution tank and the anode electrode is connected to the graphite rod. The concentration of chloride ions in the diffusion cell was measured by ISE(Ion Selective Electrode; measurable range : 5x10^{-5}～1.0 mol/*l*) every day to evaluate the chloride diffusivity.

(3) Calculation of chloride diffusivity

Fig. 2 shows the increase of chloride concentration in the diffusion cell with the time. The concentration of chloride ions reached a steady state through a transient state when the diffusion cell was applied by an electrical difference. Chloride diffusivity was calculated by Eq. (1) when the increasing rate of chloride concentration in the cell was constant. This Equation is derived from the relationship between the migration term in Nernst-Planck equation and mass flux. [14]

$$D_{migration} = \frac{RT}{zFC_1}\frac{l}{\Delta E}\frac{V}{A}\frac{dC_2}{dt} \qquad (1)$$

where,

$D_{migration}$: chloride diffusion coefficient for migration term(m^2/sec)
R : gas constant (8.314 J/mol · K)
T : absolute temperature (K)
z : electrical charge
F : Faraday constant (96,485 J/volt · mol)
C_1 : chloride concentration of cathode (mol/*l*)
l : specimen thickness (m)
ΔE : potential difference (volt)
V : volume of diffusion cell (*l*)
A : specimen area (m^2)
C_2 : chloride concentration in diffusion cell (mol/*l*)
t : elapsed time (sec)

Table 1 Chemical composition and physical properties of cement and mineral admixture

Items / Types	Chemical composition (%)						Ig. loss	Specific gravity
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3		
O P C	19.88	4.87	3.11	61.56	2.95	2.82	2.93	3.15
LHPC	22.60	3.81	4.32	62.83	2.54	2.03	1.68	3.18
SRPC	24.52	2.85	3.52	61.80	2.94	2.00	1.01	3.20
T B C	29.67	11.66	3.16	45.85	3.95	3.10	1.06	2.93
GGBF	31.88	12.64	0.39	42.46	6.38	3.63	0.65	2.92

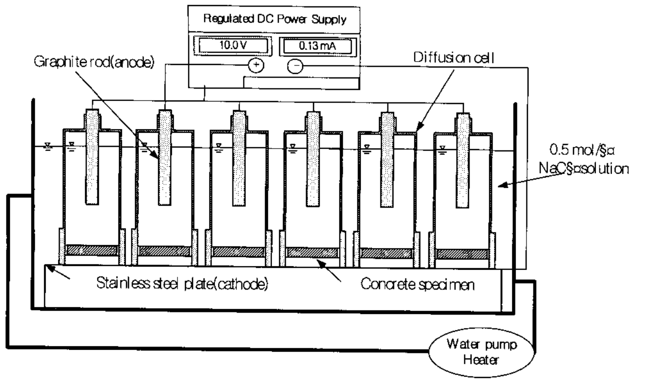

Fig. 1 Test set-up for chloride ion diffusion in concrete

2.3. Mix proportions of concrete

In order to investigate the effect of cementitious materials on the diffusivity and micro pore structure of concrete, 6 types of concretes with 0.5 water-binder ratio were studied. The mixture proportions and compressive strengths at 28 days in this work are shown in Table 2.

3. Test results and discussions

3.1. Pore volume and pore size distribution of cement matrixes

Fig. 3 shows a plot of the pore size distribution of mortar pieces from concretes consisting of the 6 types of cements. In Fig. 3, the main pore size peak of both OPC and SRPC concrete was about 30nm, however that of LHPC concrete was 70nm. It may be for this reason that LHPC cement generate comparatively low heat, therefore the rate of strength development is lower than the other cements. On the other hand, for concretes containing mineral admixtures, the pore volume below 30nm increased and for TBC concrete the pore sizes above 50nm decreased considerably.

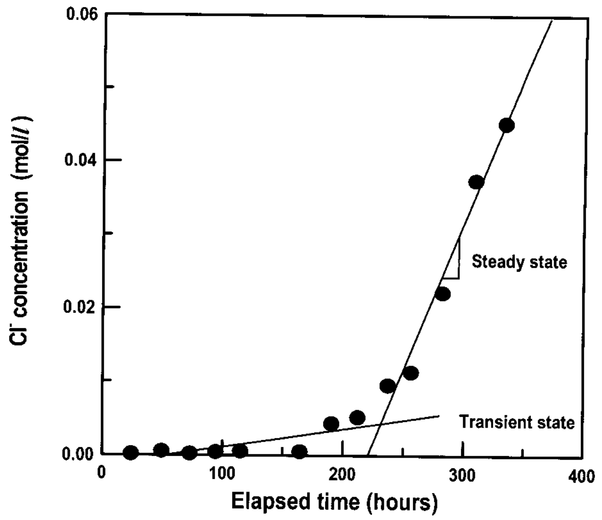

Fig. 2 Typical plot of chloride concentration in diffusion cell

The total pore volumes and median pore diameters for the 6 types of concretes are listed in Table 3. The median pore diameter is defined as the pore diameter of the 50 % of total pore volume on the cumulative pore volume plot.

The total pore volumes of LHPC and SRPC increased by 109 and 112 %, respectively, compared to the OPC. The total pore volumes of Slag 40 and TBC concrete increased by 104 and 113 %, respectively, whereas the total pore volume of Slag 60 concrete was decreased by 93 %. The median pore diameters of concretes containing the mineral admixtures were smaller than those of the OPC, SRPC and LHPC. This implies that the addition of mineral admixtures changes the pore size into fine distribution, and shifts the

Table 2 Concrete mix proportions and compressive strength

Items / Types	Slump (cm)	Air (%)	W/C (%)	S/a (%)	Unit weight(kg/m^3)					Compressive strength (kgf/cm^2)
					W	C	S	G	GGBS	
O P C	14.6	3.9	50	43	187	374	734	973	-	306
LHPC	16.3	4.5	50	43	187	374	736	975	-	246
SRPC	15.7	4.5	50	43	187	374	736	976	-	325
Slag 40	15.1	4.4	50	43	187	224	724	960	150	353
Slag 60	15.7	4.3	50	43	187	150	724	960	224	297
T B C	16.3	3.6	50	43	187	374	724	960	-	361

Table 3 Pore analysis data of cement matrixes at 28 days

Items / Types	OPC	LHPC	SRPC	Slag 40	Slag 60	TBC
Total pore volume (ml/g)	0.0931 (100)	0.1063 (108.6)	0.1040 (111.7)	0.0970 (104.2)	0.0861 (92.5)	0.1047 (112.5)
Median pore diameter (nm)	31.6	59.9	30.2	10.8	9.7	8.5

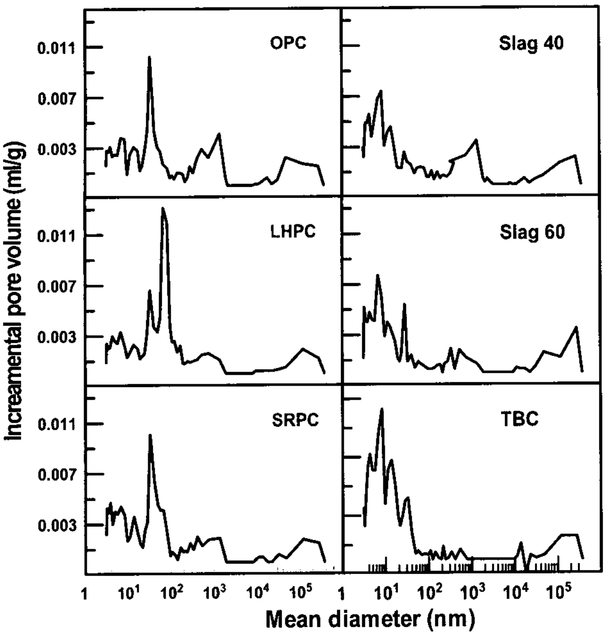

Fig. 3 Pore size distribution of cement matrixes

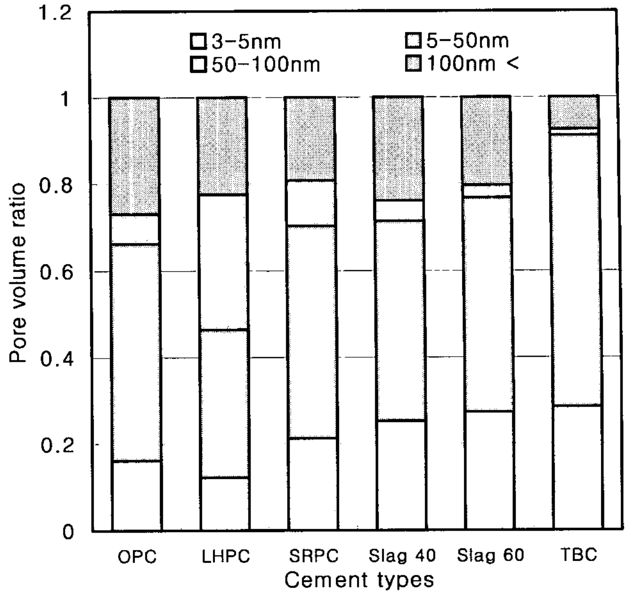

Fig. 4 Pore volume ratio of concretes

median pore diameter small, although there was not a great difference in total pore volumes between concretes with and without mineral admixtures.

The pore size distribution of cement matrix affects the characteristics of concrete and changes with the hydration degree of cement. There have been a number of classification studies on pores, but the classifications are not in agreement. Uchigawa et al.[15, 16] classified pore diameters below 3 nm as gel pores and those ranging from 3 nm ~ 30 ㎛ as capillary pores. According to their studies, an increase in gel pores decreases the permeability of ions, but an increase in total pore volume increases the permeability of ions. Mehta[17] regarded pores below 5nm in diameter as gel pores and those between 5 ~ 100 nm as capillary pores. He classified pores in the range of 5 ~ 50 nm as micro-pores, and those between 50 ~ 100 nm as macro-pores. The micro-pores affect the shrinkage and creep of the cement matrix, and the macro-pores affect the strength and permeability. Neville[18] classified pores below 2.5 nm as gel pores. On the other hand, Kumar et al.[19] classified pores with diameters ranging from 0.5 ~ 10 nm as gel pores, pores with diameters of 5 ~ 5000 nm as capillary pores and pores with diameters above entrained air as macro-pores. Though there are discrepancies among the pore classification pore systems of these researchers, there is agreement that pores with diameters above 5 ~ 10 nm are classified as capillary pores.

Fig. 4 shows the ratio of pore volume in specified ranges (3 ~ 5, 5 ~ 50, 50 ~ 100 and above 100 nm) over total volume with the pore size distribution of 6 types of concretes. For LHPC, the pore volume percentages of 5 ~ 50 and 50 ~ 100 nm over total pore volume were 34 and 31 %, respectively. The pore volume of 3 ~ 5 nm was 12 %, the lowest of all the concretes. For the rest of concretes, the pore volume of 5 ~ 50 nm range occupied about 50% without respect to the types of cements and binders. Also, the addition of mineral admixtures decreased the pore volume of 50 ~ 100 nm range, but increased the pore volume of 3 ~ 5 nm range. Compared with the OPC, for TBC, pore volume of the 5 ~ 50 nm range increased about 13 % and the pore volume below 50nm over total volume was 91 %.

3.2. Effect of pore characteristics of cement matrix on compressive strength

Fig. 5 shows the relationship between compressive strength, total pore volume and median pore diameter of concretes. There was not a significant correlation between the total pore volumes and compressive strengths. However, there was a good correlation between the median pore diameters and compressive strengths, 0.98 determinant coefficient, when the Slag 60 concrete was omitted because it considered experimental error.

The correlations between the pore volumes of pore size distribution of above 5, 50 and 100 nm range and compressive strengths are shown in Fig. 6. The determinant coefficients were 0.26, 0.67 and 0.28, respectively. It was, therefore, found that the pore volume of above 50 nm had an effect on the compressive strength of concrete.

Both Mehta and Neville reported the nearly the same results [17, 18] and Hwang et al.[20] presented similar results,

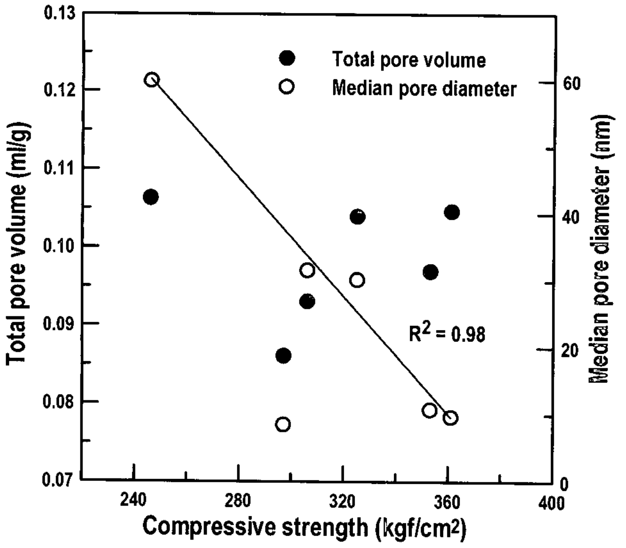

Fig. 5 Relationship between compressive strength and pore characteristics

which were obtained by comparing the measured compressive strengths and predicted compressive strengths from the capillary porosity of microstructure associated with strength development. It should be noted that the compressive strength of concrete is more influenced by the pore size distribution and a specific pore volume than by the total pore volume of cement matrix.

3.3. Effect of pore characteristics of cement matrix on chloride diffusion coefficient

Fig. 7 shows the diffusion coefficients of the 6 types of concretes at 28 days. The diffusion coefficients of OPC and SRPC were nearly identical, while the diffusion coefficient of LHPC was about two times greater than that of OPC. The percentages of diffusion coefficient of Slag 40, Slag 60 and TBC concrete over that of OPC were 64, 23 and 24 %, respectively. From these results, it can be seen that the use of mineral admixtures considerably decreases the diffusion coefficient of concrete.

The relationship between the compressive strength at 28 days and chloride diffusion coefficient is shown in Fig. 8. In general, the diffusion coefficient decreased as the compressive strength increased. The determinant coefficient was 0.57 in concrete using portland cements and 0.14 in concrete using blended cements. Consequently, it is concluded that there was a very low correlation between the diffusion coefficient and compressive strength.

Fig. 9 shows the relationship between diffusion coefficient, total pore volume and median pore diameter of concretes. There was not a significant correlation between the total pore volumes and diffusion coefficient. However,

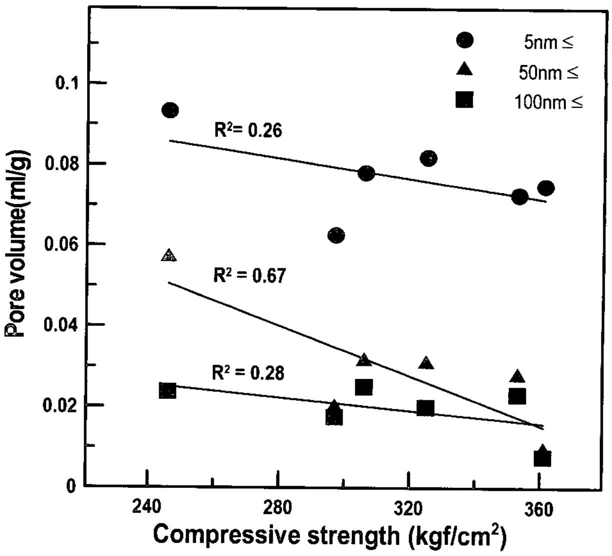

Fig. 6 Relationship between compressive strength and pore Volume

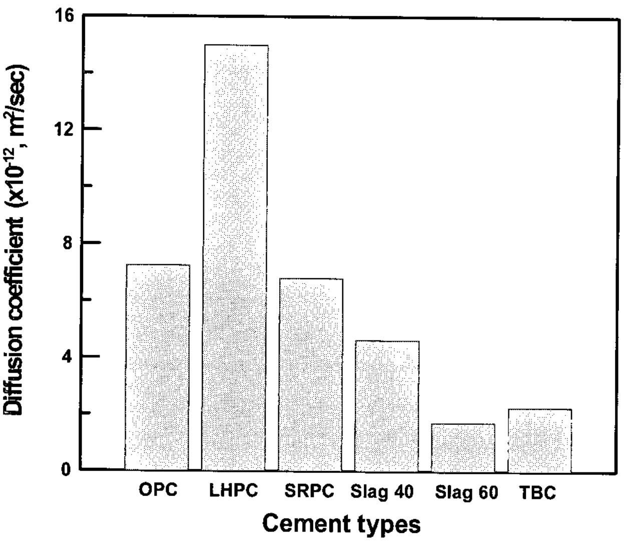

Fig. 7 Chloride diffusion coefficient of concrete mixtures at 28days

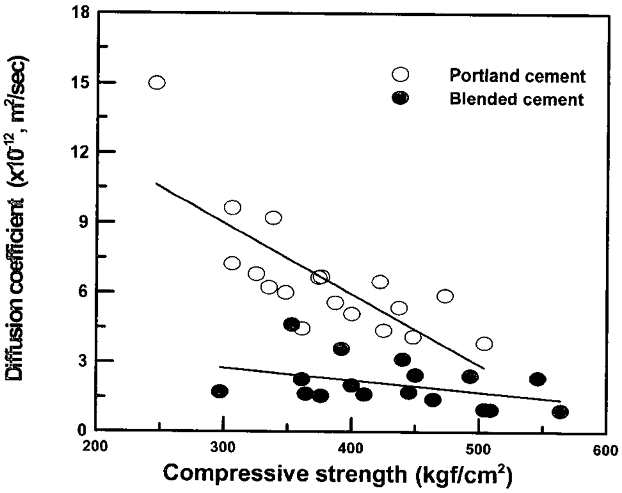

Fig. 8 Relationship between compressive strength and diffusion coefficient

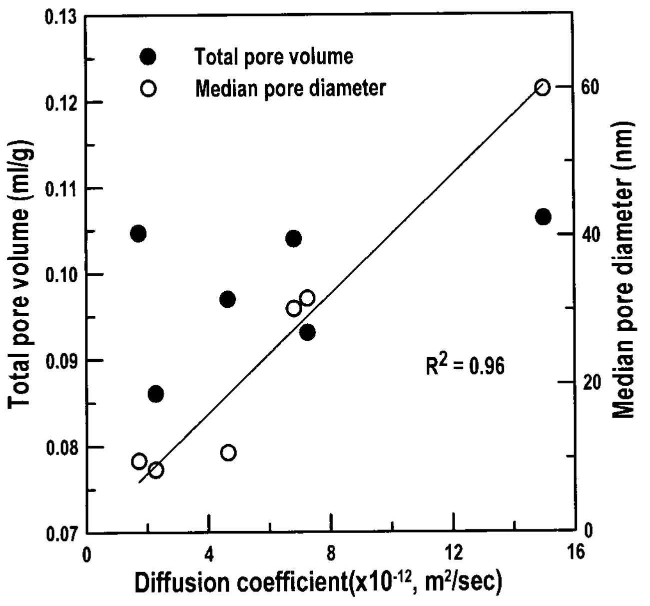

Fig. 9 Relationship between diffusion coefficient and pore characteristics

there was a good correlation, 0.96 determinant coefficient.

Besides, Fig. 10 plots the correlation between the classified pore volumes of a specific range such as above 5, 50 and 100 nm and the diffusion coefficients. As can be seen in Fig. 10, the determinant coefficient between the pore volume above 5 nm and diffusion coefficient was 0.84. The determinant coefficient between the diffusion coefficient and the pore volumes above 50 nm, was 0.93, through which the moisture including the chloride ions can easily move in and out. There was not a correlation between the pore volume above 100nm and diffusion coefficients because the determinant coefficient was 0.36.

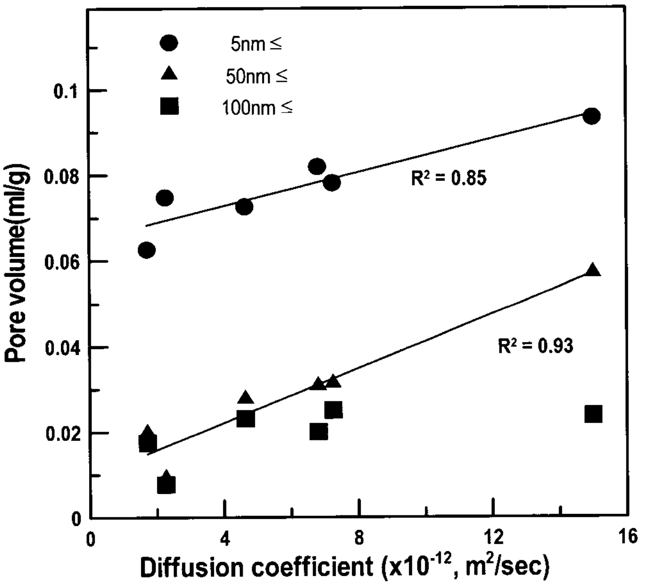

Fig. 10 Relationship between pore volume and diffusion coefficient

From these results, it was concluded that chloride diffusivity is closely related to the pore size distribution of cement matrix. This is supported by the study of Soh et al.[3], who reported that the pore volumes above 50 nm decreased the permeability of chloride into concrete. According to Dullien,[21] chloride diffusivity is influenced by porosity, pore size distribution and connectivity and tortuosity of the pores. Therefore, the reactants of the latent hydraulic reaction or pozzolan reaction of mineral admixtures makes large pores finer by a filling effect in the cement hydrates, thereby, resulting in lengthening the diffusion path of ions due to the decrease of connectivity and the increase of tortuosity of the pores. This causes a decrease in the chloride diffusion coefficient in concrete containing mineral admixtures.

4. Conclusions

The following conclusions are drawn from the present investigation.

1) From the pore size distribution of 6 types of concretes, the addition of mineral admixtures increased fine pore volumes and considerably decreased the median pore diameter. However, the change in the total pore volumes was not large. This is due to hydrates of mineral admixtures making large pores finer.
2) There was not a significant correlation between the total pore volume and compressive strength, while there was a good correlation between the median pore diameter, the pore volume above 50 nm and compressive strength. This means that in an analysis of the factors influencing the strength of concrete, considerations of the pore size distribution and a specific pore volume is more useful than simple comparison with total pore volume.
3) There was not a significant correlation between compressive strength and diffusion coefficients, while there was a good correlation between the pore volume above 50 nm and chloride diffusion coefficients. The reason why diffusion coefficient of concrete containing the mineral admixtures decreases is a decrease in the connectivity and the increase of tortuosity of pores which lengthens the diffusion path of ions.

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