

## Oxygen and Chloride Ion Diffusion in Concrete Using Silica Fume, Blast Furnace Slag and Fly Ash

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### ABSTRACT

In this study, the diffusion coefficients of oxygen and chloride ions in the hardened cementitious materials using silica fume, granulated blast-furnace slag and fly ash were measured. From the experimental results, the oxygen diffusion coefficients of various mixtures were different depended on the kinds of binder even if the pore volume was the same. In particular, the oxygen diffusion coefficients of the specimen using the mineral admixtures were smaller than that of the specimen using only the Ordinary Portland Cement. In comparison with the diffusion of oxygen gas, the diffusion of chloride ions varies markedly depending on the kind of binder. The chloride ion diffusion coefficients of various materials can be evaluated in consideration of the microstructure and the electric property of concrete.

**Keywords.** Oxygen, Chloride Ions, Diffusion, Mineral Admixture

## 1. Introduction

It is important for prediction of the durability of the concrete structure to evaluate the mass transport in concrete. The mass transport in concrete is affected mainly by the microstructure and the electric property of concrete. Therefore, it is affected by mineral admixtures, such as silica fume, granulated blast-furnace slag and fly ash. However, the effect of mineral admixtures on the microstructure and the electric property of concrete has not been clarified. The effects of the microstructure and the electric property on mass transport should be evaluated independently for a quantitative understanding of the effect of mineral admixtures.

In this study, diffusion coefficients of oxygen and chloride ions in the hardened cementitious paste and mortar using silica fume, granulated blast-furnace slag and fly ash were measured. The relation between oxygen diffusion coefficient and chloride ion diffusion coefficient and the effects of the microstructure and the electric property on diffusion coefficient were studied.

## 2. Experimental Procedure

### 2.1 Materials and specimen

In this study, an ordinary Portland Cement (N) was used. Two types of silica fume (Sa and Sb), a granulated blast-furnace slag (B) and a fly ash (F) and were used as mineral admixtures. The physical and chemical properties of the cement and the mineral admixtures are shown in Table. 1.

Paste specimens and mortar specimens were used in the experiments. The mix proportions of the paste and the mortar are shown in Table. 2. The paste and the mortar were cast in 40\*30\*5 mm molds. The paste specimens removed from the molds after 3 to 5 days later from casting, and the mortar specimens were removed from molds after one day later from casting. All specimens were cured in a completely sealed plastic bag at 20C after demold. The curing period was 28 days. Only the pastes using fly ash were cured for 91 days. Some steam cured mortar specimens (STM) were also used in the experiments. The steam curing condition is shown in Fig.1

Table 1 Physical properties and chemical compositions of materials

	Density (g/cm <sup>3</sup> )	Blaine (cm <sup>2</sup> /g)	Chemical composition (%)								
			SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cl
N	3.16	3090	20.98	5.28	2.63	64.64	2.11	2	0.32	0.48	0.03
B	2.88	4010	32.58	12.85	0.25	42.33	5.95	2.08	0.22	0.35	-
F	2.14	3500	56.65	27.63	4.4	3.58	1.2	-	0.48	0.46	-
S <sub>a</sub>	2.2	-	96.5	0.46	0.13	0.18	0.37	-	0.22	0.86	
S <sub>b</sub>	2.2	-	89.32	0.3	0.95	0.69	<1.6	0.37	0.85	3.02	0.12

Table 2 Mix proportions of paste and mortar

paste				mortar				
Binder		Water to binder ratio (%)	Replacement ratio of mineral admixture (%)	Binder		Water to binder ratio (%)	B/(N+B) (%)	S/(N+B) (%)
N	N35	35	-	N	N35	35	0	0
	N45	45			N45	45		
	N55	55			N55	55		
	N65	65		N+B	B35-40	35	40	
N+B	B55-35	55	B45-40		45			
	B55-50	55	B55-40		55			
	B45-70	45	70					
N+F	F45-30	45	30	N+B+Sb	BS35-40-4	35	40	4
	F55-30	55			BS45-40-4	45		
	F65-30	65			BS55-40-4	55		
	N+Sa	S45-8		45	8			

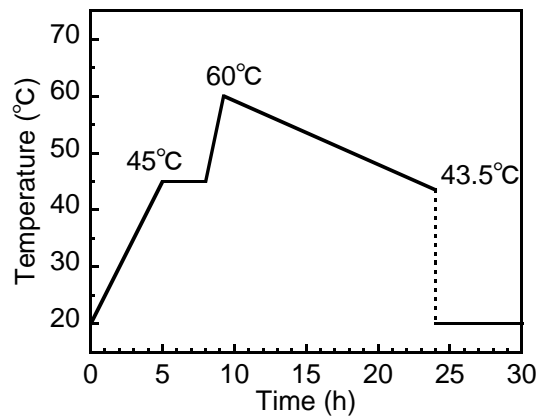


Fig.1 Temperature history of steam curing

## 2.2 Test method

### (1) Microstructure

The pore volume of the specimens was measured by Archimedes' principle after initial curing. The specimens were dried until the weight of the specimens became constant. The drying conditions were 50C, and 20C air and 45% relative humidity. Pore size distribution in the range of 6 nm to 200 μm in diameter of pore was measured by mercury intrusion porosimetry.

### (2) Diffusion coefficient of O<sub>2</sub>

The oxygen diffusion test was performed according to earlier research (Shirakawa 1999). The 40\*30\*5 mm thin plate specimens were dried at 50C or 20C-45%RH until the weight of the specimen was constant. The apparatus consists of two diffusion cells separated

by a thin stainless plate and the thin plate specimen. The oxygen diffusion coefficient was calculated from the flux of O<sub>2</sub> in the steady state. (Kikuchi, 2011).

### (3) Diffusion coefficient of Cl<sup>-</sup>

The chloride ion diffusion test was performed according to the JSCE standard test method (Japan Society of Civil Engineers 2004). However, no DC potential was applied in order to examine the diffusion due to concentration gradient under natural condition. The dimensions of the specimen were the same as the specimen used for oxygen diffusion test. In order to saturate the specimen with water, vacuum saturation was carried out. After saturation, the specimen was mounted diffusion cell. Two sections separated by the specimen were filled with NaOH solution and NaCl solution respectively. NaOH solution concentration was 0.3 mol/L. Test temperature was 20°C. At defined times, the concentration of Cl<sup>-</sup> in NaOH solution was measured. The chloride diffusion coefficient was calculated from the flux of Cl<sup>-</sup> in the steady state.

## 3. Experimental results and Discussions

### 3.1 Oxygen diffusion coefficient of paste and mortar using mineral admixtures

Fig. 2 shows the relation between empty pore volume and oxygen diffusion coefficient. Empty pore is defined as the pore which is not filled with water. The empty pore volume is measured by Archimedes' principle. A higher empty pore volume tends to lead a higher oxygen diffusion coefficient. However, the oxygen diffusion coefficients were different depended on the kinds of binder even if the empty pore volume was the same. When the empty pore volume was the same, kind of the binders in this study were ranked in order of oxygen diffusion coefficient from lowest to highest as N+B+S<N+F<N+S ≐ N+B<N. The values of the oxygen diffusion coefficient and the empty pore volume of the paste specimens were different from those of the mortar specimens. However, the experimental results obtained from the paste specimens and the mortar specimens were the same tendency.

It is impossible to estimate the oxygen diffusion coefficient in hardened paste based only on the empty pore volume. This may be explained by the fact that the character of microstructure, such as tortuosity, is different even if the pore volume is the same. Therefore, in this study, the tortuosity of oxygen diffusion, “τ<sub>O<sub>2</sub></sub>”, was calculated from oxygen diffusion coefficient.

The oxygen diffusion coefficient through the porous medium, such as hardened cementitious paste and mortar, can be related with the oxygen effective diffusion coefficient in pores of the porous medium as Eq.(1) (Kobayashi 1991).

$$D_{O_2} = \frac{1}{\tau_{O_2}} D \quad (1)$$

Where τ<sub>O<sub>2</sub></sub> is the tortuosity of oxygen diffusion, D is the oxygen effective diffusion coefficient in pores of porous medium. In this study, D is calculated based on the parallel pore model (Kikuchi, 2011).

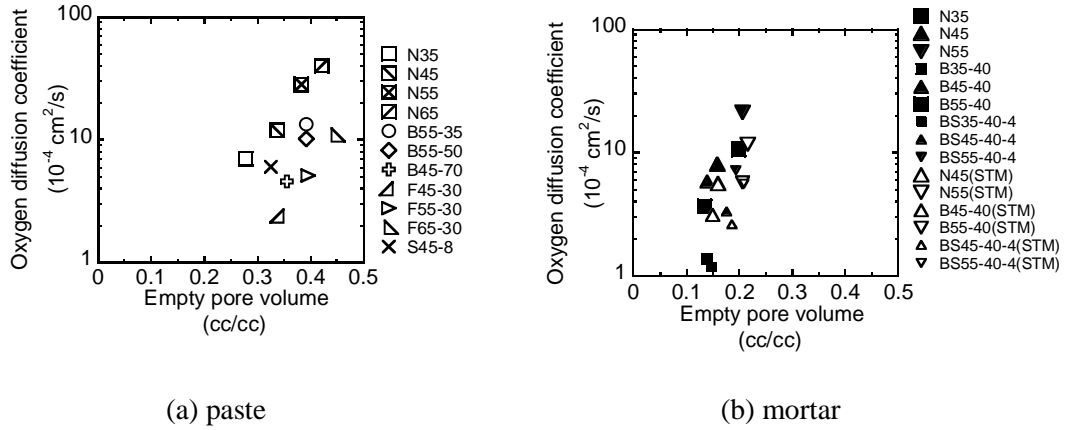


Fig. 2 Relation between empty pore volume and oxygen diffusion coefficient

### 3.2 Relation between oxygen diffusion coefficient and chloride ion diffusion coefficient

The relationship between the chloride ion diffusion coefficient and the oxygen diffusion coefficient is shown in Fig. 3. A higher oxygen diffusion coefficient tends to lead a higher chloride ion diffusion coefficient. However, when the binder type was different, the value of the chloride ion diffusion coefficient differs even if the oxygen diffusion coefficient is the same. The relationships between oxygen diffusion coefficient and chloride ion diffusion coefficient were linear on the logarithmic scale as shown in Fig.3. In Fig.3 (a), the relation between oxygen diffusion coefficient and chloride ion diffusion coefficient can be divided into two categories, such as the N and N+F group, and the N+B and N+S group. When the oxygen diffusion coefficient was the same, chloride ion diffusion coefficients of N+B and N+S were lower than that of N and N+F. In the case of the mortar specimen, the effect of the binder type was smaller than that of the paste specimen. The oxygen diffusion coefficients of N+B and N+B+S were slightly lower than N. On the contrary, the oxygen diffusion coefficients of N+B(STM) and N+B+S(STM) were slightly higher than N.

### 3.3 Effect of electric action on chloride ion diffusion

The effect of the electric action on chloride diffusion may be affected by the binder type. Previous studies, for example (Jougnot 2009), have suggested that the charge of pore surface affects the diffusion of ions, and if the pore surface charged negatively, the diffusion of anion, such as chloride ion, is inhibited.

In this study, the tortuosity  $\tau_{Cl}$  of the chloride ion diffusion were calculated in order to consider the influence of the electric action by the pore surface charge on chloride ion diffusion. The chloride ion diffusion coefficient can be expressed as follow using the  $\tau_{Cl}$ , the porosity  $\varepsilon$ , and the self-diffusion coefficient of chloride ion  $D^*$ .

$$D_{Cl} = \varepsilon \frac{1}{\tau_{Cl}^2} D^* \quad (6)$$

Using the measured chloride ion diffusion coefficient  $D_{Cl}$  and porosity, the  $\tau_{Cl}$  are calculated. The value of self-diffusion coefficient of chloride ion is used 1.772 at 25C in 1.0 mol/L NaCl solution. The  $\tau_{Cl}$  and the  $\tau_{O_2}$  represent the diffusion pass length of chloride ion and oxygen respectively. The relationship between  $\tau_{Cl}$  and  $\tau_{O_2}$  is shown in Fig. 4. From Fig. 4, the  $\tau_{Cl}$  is greater than the  $\tau_{O_2}$ . Furthermore, the  $\tau_{Cl}/\tau_{O_2}$  depends on the type of binder. The values of  $\tau_{Cl}/\tau_{O_2}$  of N+B, N+S and N+B+S were higher than those of N and the values of the  $\tau_{Cl}/\tau_{O_2}$  of steam cured mortar were lower than those of N. Therefore, it is suggested that the difference of  $\tau_{Cl}/\tau_{O_2}$  is caused by the effect of electric action.

The effect of the charge of pore surface on the ion diffusion has been studied by Friedmann et al. (Friedmann. 2008). A result of their research is shown in Fig. 5. The increasing the value of  $K_{ct}/K_{co}$  means that the flux of coions and that of counterions will be attenuated and amplified compared to the flux in the bulk solution respectively. It can be seen in Fig. 5 that  $K_{ct}/K_{co}$  increases sharply in the pore which diameter range of below 6 nm. Therefore, it means that the flux of coions becomes lower sharply.

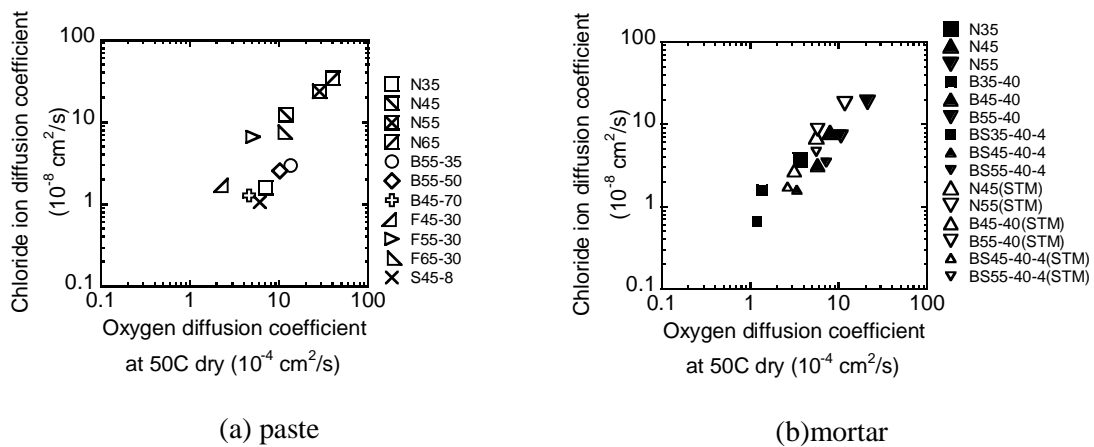


Fig.3 Relation between oxygen diffusion coefficient and chloride diffusion coefficient

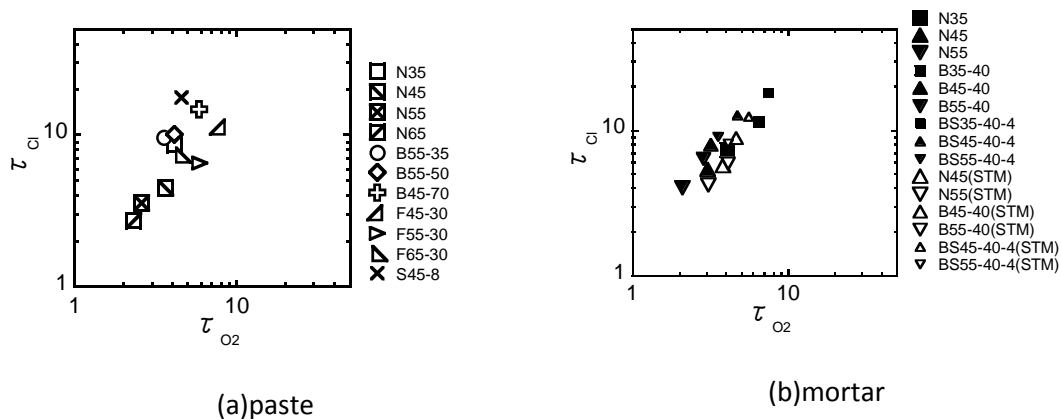


Fig.4 Relation between  $\tau_{Cl}$  and  $\tau_{O_2}$

The pore surface of hardened cementitious materials is usually charged positively. In the case that the chloride ions penetrate into pore solution, the electric potential of pore surface would change from positive to negative by the adsorption of the chloride ion. Considering the result of Friedmann et al (Friedmann. 2008), the diffusion of chloride ion will be inhibited in the pore which has diameter below 6 nm, because the pore surface is charged negatively by the adsorption of the chloride ion. In contrast, oxygen can diffuse in the pore which has diameter below 6 nm. Therefore, the diffusion path length of chloride ion would be longer than that of oxygen as shown in Fig.4. The  $\tau_{Cl}/\tau_{O_2}$  means the extended ratio of the diffusion path length of oxygen to that of chloride ion. The larger the volume of the pore which has diameter below 6 nm, the greater the value of  $\tau_{Cl}/\tau_{O_2}$ . Figs.6 show the relationship between  $\tau_{Cl}/\tau_{O_2}$  and the pore volume of the pore which has diameter below 6 nm, " $V_{\leq 6nm}$ ".  $V_{\leq 6nm}$  has a high correlation with the  $\tau_{Cl}/\tau_{O_2}$  independent of the type of binder, presence of fine aggregate and curing condition.

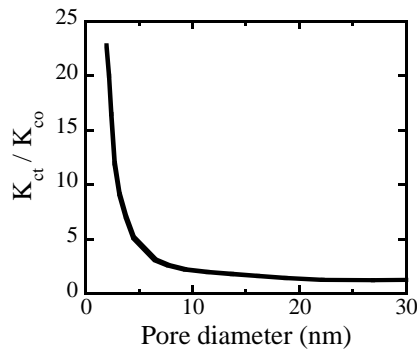


Fig. 5. Relation between pore diameter and  $K_{ct}/K_{co}$

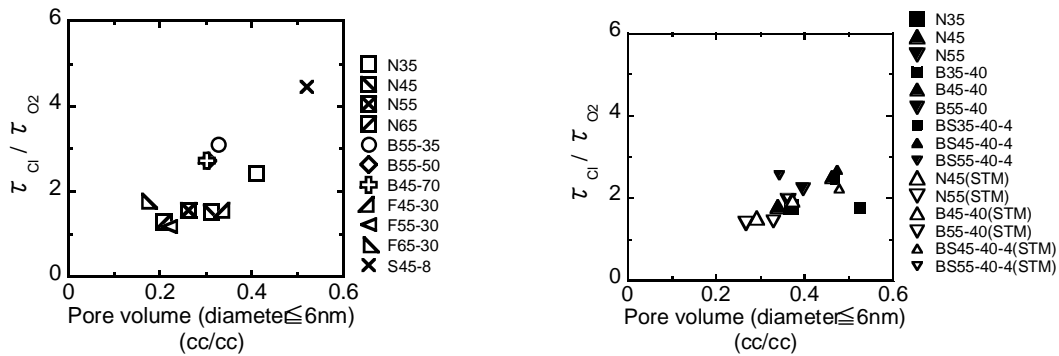


Fig. 6 Relation between  $V_{\leq 6nm}$  and  $\tau_{Cl}/\tau_{O_2}$

The effect of drying condition on the empty pore volume and the oxygen diffusion coefficient of the paste specimen was studied. Fig. 7 shows the relation between the pore volumes of the specimens dried at 50C and of those of the specimens dried at 20C-45%RH. The pore volumes of the 50C-dry specimens were larger than those of the 45%RH-dry

specimens. This means 50C-dry is stronger drying condition than 45%RH and the empty pore volume of the 50C-dry specimen is larger than that of the 45%RH-dry specimen. Fig.8 shows the relation between the empty pore volume of the 45%RH-dry specimens and the pore volume which diameter range of over 6 nm. It is confirmed that the 45%RH-dry pore volume is equal to the pore volume which diameter range of over 6 nm.

Figs. 9 show the relations between the oxygen diffusion coefficient and the chloride diffusion coefficient. Fig.9(a) shows the oxygen diffusion coefficient of the 50C-dry specimen and Fig.9(b) shows the oxygen diffusion coefficient of the 45%RH-dry specimen. When the specimen was dried at 45%RH, the correlation between the oxygen diffusion coefficient and the chloride diffusion coefficient was stronger. This means that the diffusion of chloride ions takes place in the pores which diameter range of over 6 nm indirectly.

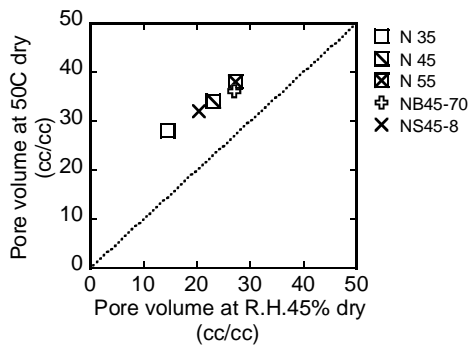


Fig.7 Relation between the 45%RH-dry pore volume and the 50C-dry pore volume

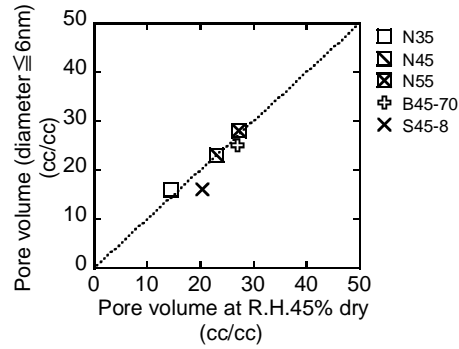
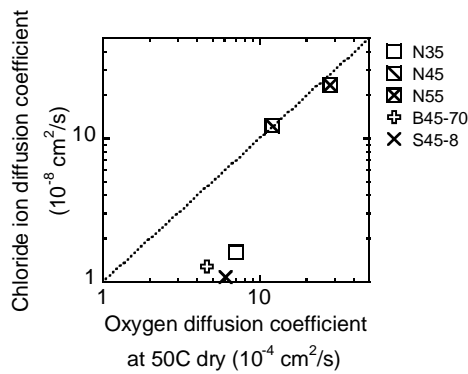
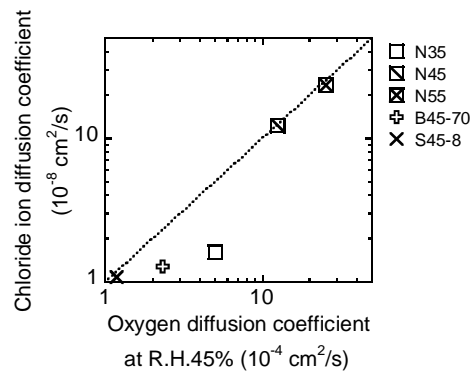


Fig.8 Relation between the 45%RH-dry pore volume and the pore volume which diameter range of over 6nm



(a)



(b)

Fig.9 Relation between oxygen diffusion coefficient and chloride diffusion coefficient.



### 3.4 Numerical simulation of the change of the tortuosity by the action of charged pore surface

In this paper, the numerical simulation of the change of tortuosity by the action of charged pore surface was done. In particular, the diffusion path lengths of oxygen and chloride ion were simulated, and the both were compared. When performing the numerical simulation, the following conditions were defined.

The mass transfer media in the simulation was 2000 \* 2000 two dimensional lattices. Fig. 10 shows the schematic figure of the mass transport simulation. The each line of mass transfer media was reflected from the measurement results of the pore volume and the pore size distribution in the hardened cementitious materials. The pores with various pore diameters were randomly arranged at each line. The simulation scheme of mass transport was simple and the mass transport was one direction transport. In the case of oxygen diffusion, oxygen could pass through all pores. In contrast, it was defined that chloride ions could not pass through the pores which has diameter below 6nm by the electric action of pore surface (Friedmann. 2008). The tortuosity of oxygen and chloride ion in the transfer media with the same pore structure condition was calculated by the simulation.

Fig. 11 shows the relationship between the pore volume which has diameter below 6nm and  $\tau_{Cl}/\tau_{O_2}$  of N35, N45, B45-70 and S45-8 which calculated by the simulation. From this figure, it shows the same tendency of Fig. 6.

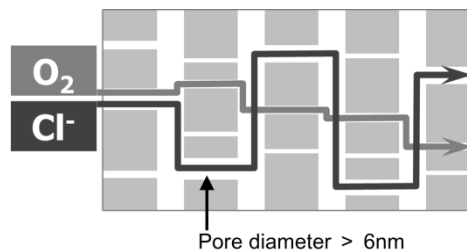


Fig. 10 The schematic figure of the mass transport simulation

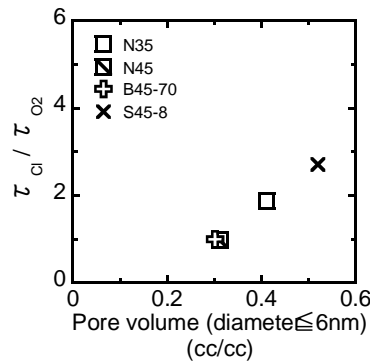


Fig.11 Relation between  $V_{\leq 6nm}$  and  $\tau_{Cl}/\tau_{O_2}$  obtained from the numerical simulation

## CONCLUSIONS

In this study, the diffusion coefficients of the oxygen and the chloride ion of paste and mortar specimens using mineral admixtures. The tortuosities of oxygen diffusion  $\tau_{O_2}$  and chloride ion diffusion  $\tau_{Cl}$  were calculated based on the diffusion coefficients of the oxygen and the chloride ion respectively. The effect of the electric property on chloride ion diffusion was studied by comparing oxygen diffusion with chloride ion diffusion. The conclusions of this study are below.

- Mineral admixtures such as silica fume, blast furnace slag and fly ash were effective to control mass transport in hardened cementitious materials.
- The  $\tau_{Cl}/\tau_{O_2}$  can be correlated with the volume of pore which is below 6nm in diameter, " $V_{\leq 6nm}$ " independent of the type of binder, fine aggregate and curing condition. When the  $V_{\leq 6nm}$  is increased, the chloride diffusion path length is longer than the oxygen diffusion path length, because the chloride ion diffusion is affected by the electric action of the charged pore surface at the narrow pores.
- The numerical simulation in consideration of pore size distribution and the effect of the electric property of pore surface is useful to evaluate the  $\tau_{Cl}/\tau_{O_2}$  of the specimen using mineral admixtures.

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