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# A STUDY ON THE FACTORS AFFECTING ELECTRO-MIGRATION CHARACTERISTIC OF CHLORIDE IONS IN CONCRETE

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As one of the methods to evaluate the durability performance of reinforced concrete structure for the deterioration due to chloride attack, there is a migration test method. The effective diffusion coefficient by migration test method fluctuates with changes in the pore structure of concrete. In this study, focused on the changes of the pore structure with elapse of age of concrete, the objective of this study is to assess the influence exerted on electro-migration characteristic caused by the type of aggregates and with the condition of early age curing. It is confirmed that the resistibility to the movement by the migration test method of the chloride ion was increased by using non-ferrous slag fine aggregates. In the test specimen using sandstone of 40-65% of water-cement ratio, it is presumed that the increase in the effective diffusion coefficient of chloride ion is caused by the fact that the volume of continuous pore or pore size by the curing method and age of concrete become bigger.

*Keywords*: Reinforced concrete, Chloride attack, Effective diffusion coefficient, Pore structure, Type of aggregates, Non-ferrous slag, Curing condition, Age of concrete.

## 1 INTRODUCTION

Degradation of reinforced concrete structure owing to chloride attack is a phenomenon causing reinforcement corrosion by penetrating of chloride ions in concrete and leading to the deterioration in performance of structure such as safety. Verification of durability performance against chloride attack of reinforced concrete structure predicts chloride ions concentration at location of reinforcement in order to determine the presence or absence of corrosion occurrence of concrete. Based on Fick's diffusion law, chloride ions concentration distribution of cover concrete is predicted by using diffusion coefficient of chloride ions.

As one of the effective methods to obtain the diffusion coefficient of concrete, it is established that the method for estimating an effective diffusion coefficient of chloride ions in concrete by means of an electro-migration phenomenon (JSCE 2013). An effective diffusion coefficient obtained by the electro-migration indicates the easiness of electro-migration of an ion existing in the pore solution of concrete. It is different from an apparent diffusion coefficient that shows the diffusion rate of moving in the pore solution by a driving force from the concentration gradient. However, this method is very effective in evaluating the diffusion performance of concrete in a short time.

The purpose of this study is to assess the influence exerted on electro-migration characterization, focused on the type of the fine aggregates using in concrete and the condition of early age curing of concrete, from the viewpoint of pore structure in concrete. In addition, the effective diffusion coefficient obtained by migration test is compared with an apparent diffusion coefficient obtained by the immersion test.

## 2 EXPERIMENTAL OUTLINE

### 2.1 Materials and Specimens

Ordinary Portland cement was used. Table 1 shows the physical property of aggregates used in this experiment. Copper slag fine aggregates and manganese slag fine aggregates were used for non-iron slag fine aggregates. Table 2 shows the mix proportions of concrete. In the case (1), fine aggregates ratio was 48%. Non-ferrous slag fine aggregates replaced 30% natural aggregates in a volume ratio. In the case (2), sand-total aggregates ratio was 46%.

The concrete curing were comprised of two ways; one is that the concrete was released for 1 day and cured in water until 28 days and the other was that released for 3 days and cured in t air curing until 28 days after casting the concrete respectively. In the case (1), specimens are tested at age of 28 days, and in the case (2) specimens are tested at age of 28 days, 6 months and 1 year.

Table 1. Properties of aggregate.

| Aggregate | Designation | Types | Density ($g/cm^3$) | Absorption capacity (%) |
|---|---|---|---|---|
| Fine | CSS | Crushed sand obtained from sandstone | 2.61 | 1.06 |
| | CSA | Crushed sand obtained from andesite | 2.60 | 1.74 |
| | CSL | Crushed sand obtained from limestone | 2.66 | 0.58 |
| | CUS | Copper slag fine aggregate | 3.55 | 0.04 |
| | MNS | Manganese slag fine aggregate | 2.91 | 0.97 |
| Coarse | CSG | Crushed stone obtained from sandstone | 2.63 | 1.15 |
| | CAG | Crushed stone obtained from andesite | 2.61 | 1.97 |

Table 2. Mix Proportions of concrete.

| Case | Name of mix | W/C (%) | Unit weight ($kg/m^3$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Water | Cement | Aggregate | | | | | | |
| | | | | | Fine | | | | | Coarse | |
| | | | | | CSS | CSA | CSL | CUS | MNS | CSG | CAG |
| (1) | SOPC | 55 | 175 | 318 | 851 | | | | | 929 | |
| | AOPC | 55 | 175 | 318 | | 847 | | | | | 922 |
| | SCUS | 55 | 175 | 318 | 595 | | | 347 | | 929 | |
| | SMNS | 55 | 175 | 318 | 595 | | | | 285 | 929 | |
| | ACUS | 55 | 175 | 318 | | 593 | | 347 | | | 922 |
| | AMNS | 55 | 175 | 318 | | 593 | | | 285 | | 922 |
| (2) | SOPC40 | 40 | 175 | 438 | 382 | | 394 | | | 912 | |
| | SOPC50 | 50 | 175 | 350 | 395 | | 412 | | | 957 | |
| | SOPC65 | 65 | 175 | 269 | 428 | | 428 | | | 994 | |

### 2.2 Outline of Migration Test and Immersion Test

The migration test method was conducted according to JSCE-G 571-2013 (JSCE 2013) using the device in Figure 1. A disc specimen used for the migration test was shaped into 50 mm thickness by cutting off a 50mm from the placed face by a diamond cutter from $\varphi 100\times 200$mm cylindrical specimen. The sealed disc specimen was immersed in the vacuum desiccator injected distilled water, and depressurized with a vacuum pump for 24 hours and was saturated with water. The following parameters were measured; current value, a potential difference of the surface of the specimen, solution temperature and chloride ions concentration of cathode side and anode side every 24 hours. When the chloride ions concentration of the anode side solution was changed with time and the increase rate of chloride ions concentration became the same by measuring at least 5 times, it was judged to be steady state. Then, effective diffusion coefficient ($D_e$) of chloride ions of concrete (cm$^2$/yaer) was calculated as follows:

$$D_e = \frac{J_{cl} RTL}{|Z_{cl}| F C_{cl} (\Delta E - \Delta E_c)} \times 100 \tag{1}$$

where, $J_{cl}$ : flux of chloride ion under the steady state (mol/(cm$^2$·year)), $R$: gas constant (8.31J/(mol·K)), $T$: absolute temperature (K), $Z_{cl}$: charge of chloride ion (= -1), $F$: Faraday constant (96500C/mol), $C_{cl}$: chloride ions concentration of cathode side (mol/$l$)、$\Delta E - \Delta E_c$: potential between the test specimen surfaces (V), $L$: specimen thickness (mm).

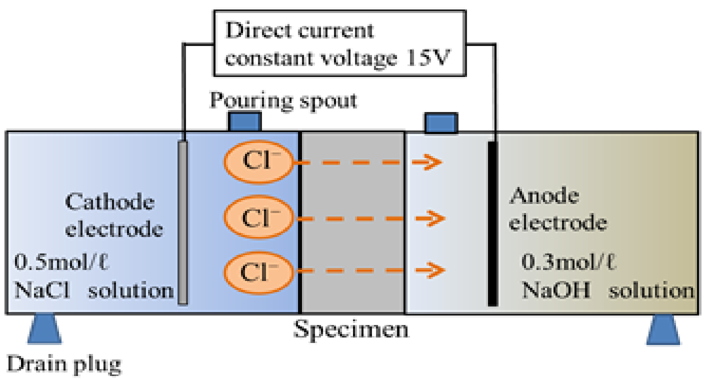


Figure 1. Apparatus for migration test.

The immersion test method calculates apparent diffusion coefficient of chloride ions under non-steady state by immersing the concrete in salt water for 90 days. Two prism specimens of 100×100×400mm are made for each mix proportion; one is cured in water and the other is cured in air 28 days. The surface concrete was left immersed and the others were sealed. Then, the surface was immersed into the salt water having 3% concentration. Subsequently, small specimens were cut 5mm to 25mm down from the surface, and chloride ions contents were measured. Apparent diffusion coefficient was calculated from the chloride ions content.

## 3 TEST RESULTS AND DISCUSSION

### 3.1 Effects of Type of Aggregate and Measuring Age on Electro-migration Characteristic

Figure 2 shows the effects between type of fine aggregates and curing condition on the effective diffusion coefficient. Based on the concrete used sandstone (CSS and CSG), the effective diffusion coefficient of the concrete remained virtually unchanged while the coarse aggregates was replaced with coarse aggregates from andesite or was under air curing. However, as 30% sandstone fine aggregates was replaced with manganese slag fine aggregates, the effective diffusion coefficient decreased by about 20%. On the other hand, when 30% sandstone fine aggregates was replaced with copper slag fine aggregate, it didn't show an influence on the effective diffusion coefficient. However, when aggregates from andesite was replaced with copper slag fine aggregates, the effective diffusion coefficient decreased around 16%.

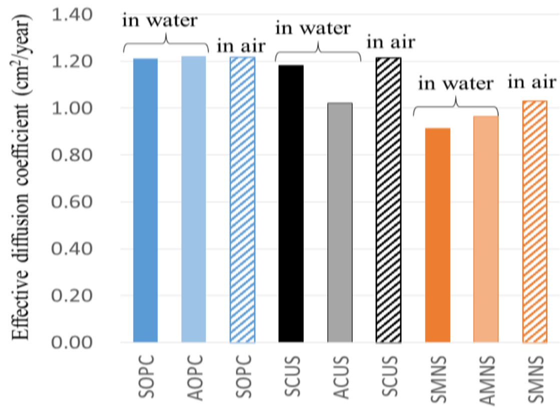


Figure 2. Effective diffusion coefficient of concrete using non-iron slag fine aggregate.

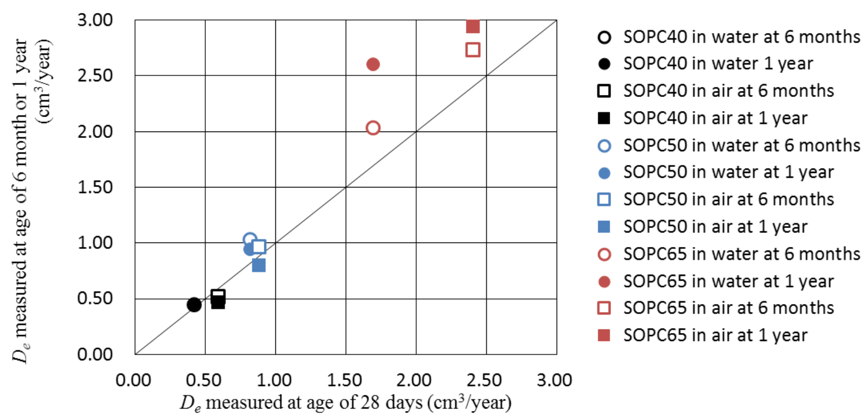


Figure 3. Effect of measured age on effective diffusion coefficient.

Figure 3 shows the result both age of 6 months and 1 year compared to the one of 28 days. For concrete with W/C40% and W/C50%, the effective diffusion coefficient of concrete after the lapse of 6 months or 1 year is almost the same as that of concrete measured at 28 days. However, for concrete with W/C65%, the effective diffusion coefficient of concrete cured in air become larger than that of concrete cued in water. Furthermore, the effective diffusion coefficient increases with the lapse of measuring gage.

### 3.2 Consideration from the Viewpoint of Pore Structure in Concrete

Figure 4 shows the relationship between pore volume measured at 28days and that measured at 1 year. The pore volume was measured by a mercury penetration method. Compared to pore volume measured by age of 28 days and 1 year specimens, the result showed no differences between the age of 28 and 1 year specimens of W/C 40%. Besides except for the result which was W/C50% under air curing, pore volume became larger after the elapse of 1 year for the age of concrete. Especially, it was noted that pore volume became larger with elapse of age of concrete in each curing for the specimens of W/C65%.

Figure 5 shows the relationship between the effective diffusion coefficient and pore volume. It was confirmed that large water-cement ratio results in large effective diffusion coefficient.

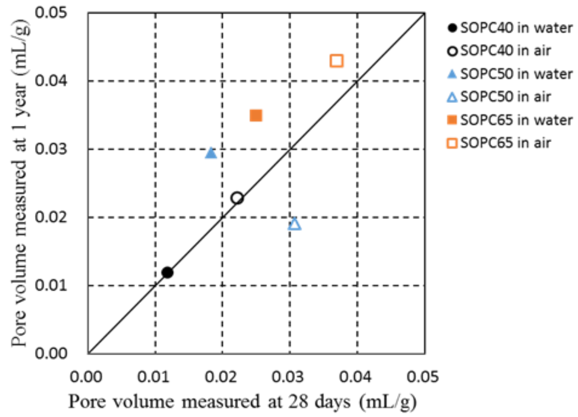


Figure 4. Relationship between pore volume measured at 28days and that measured at 1 year.

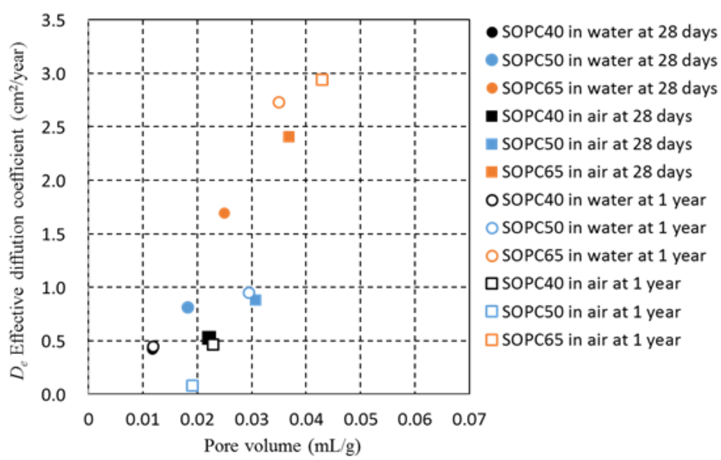


Figure 5. Relationship between pore volume and effective diffusion coefficient.

### 3.3 Relation between Apparent Diffusion Coefficient and Effective Diffusion Coefficient

Figure 6 shows the apparent diffusion coefficient by the immersion method and the effective diffusion coefficient of age of 28 days. As it is commonly known, apparent diffusion coefficient of concrete became small under the water-curing than air curing. Moreover focused on the differences from fine aggregates, in spite of the same water-cement ratio, apparent diffusion coefficient became smaller about 67.3% and 65.1% respectively by replacing 30% manganese slag fine aggregate with copper slag fine aggregates in water curing. Relatively, there was good correlation between the apparent diffusion coefficient and the effective diffusion coefficient including the result from the concrete using non-ferrous slag fine aggregates.

Previous study (JSCE 2013) has been reported that the apparent diffusion coefficient is calculated from the effective diffusion coefficient obtained from electro-migration test as follows:

$$D_a = k_1 \cdot k_2 D_e \qquad (2)$$

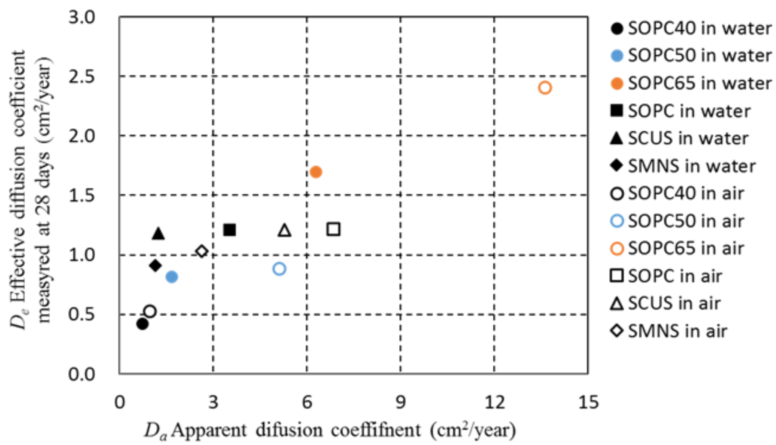


Figure 6. Relationship between apparent diffusion coefficient and effective diffusion coefficient.

Then, $k_1$: function with the balance of chloride ions concentration on the surface of the concrete side, cathode side and solution side respectively. $k_2$: coefficient with solidification phenomenon of chloride ions in the cement hydrates. The coefficient $k_1 \cdot k_2$ of concrete under water curing became larger when the water-cement ratio became larger. Besides coefficient $k_1 \cdot k_2$ became larger when it was under air curing except for 40%water-cement ratio. It is noted that coefficient $k_1$ theoretically coincides with the inverse of porosity of concrete. However, it came out the opposite of the result the pore volume shown in Figure 5. It is noted that coefficient $k_2$ is determined based on the ratio of fixed chloride ions concentration to all chloride ions concentration, from this reason it seemed that the concrete W/C50% and 65% under air curing has small amount of chloride ions in the cement hydrates. On the other hand, coefficient $k_1 \cdot k_2$ used non-ferrous slag fine aggregates was smaller than that of the natural aggregates concrete.

## 4 CONCLUSIONS

The conclusions derived from this experimental program are summarized as follows:

1. It was confirmed that using non-ferrous slag fine aggregates contributed to the improved resistance of the movement by the electro-migration of chloride ions.
2. For concrete with W/C40%, the diffusion coefficient of chloride ions remained virtually unchanged while the initial curing was changed from water curing to air curing, moreover even if the test launched 1 year later it was almost unchanged.
3. For concrete with W/C50% and 65%, the diffusion coefficient of chloride ions became larger when the initial curing was changed from water curing to air curing.
4. The effects of initial curing condition and age of concrete on the diffusion coefficient of chloride ions of concrete without ferrous slag fine aggregates can be explained from the viewpoint of changes of pore structure in concrete.

## References

Japan Society of Civil Engineers (JSCE), *STANDARD SPECIFICATINS FOR CONCRETE STRUCTURES – 2013 Test Methods and Specifications*, Maruzen Publishing Co. Ltd, Tokyo, 2013.