

## Consideration about Chloride Ion Diffusion Coefficient Estimated by Electric Resistivity of Concrete Exposed in Tidal Zone

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### ABSTRACT

It is well known that the electric resistivity of concrete is one of the useful durability indicators for chloride induced deterioration of concrete structures. In this study, the influence of air temperature and relative water content ratio in concrete on some measuring results of the electric resistivity was investigated by using the concrete specimens which were exposed in tidal zone. In addition, this paper compared the apparent chloride ion diffusion coefficient of the concrete specimens with the estimation chloride ion diffusion coefficient evaluated by some measuring results of the electric resistivity and the estimation formula which was introduced from Nernst-Planck equation. As a result, it was obvious that high temperature or high relative water content ratio made the electric resistivity low. Moreover, it was confirmed that there was a good correlation between the estimation chloride ion diffusion coefficient and the apparent chloride ion diffusion coefficient.

**Keywords.** Diffusion Coefficient, Electric Resistivity, Chloride Ion, Nernst-Planck Equation, Relative Water Content Ratio

### INTRODUCTION

**Background.** It is well known that the electric resistivity of concrete is one of the useful durability indicators for chloride induced deterioration of concrete structures. The previous studies proposed the criteria for interpretation of electric resistivity measurement values considering with the relationship between the risk of steel corrosion and the electric resistivity (BRE Digests 434, 1998; Polder et al., 2000). Similarly, some previous study pointed to the relationship between electric resistivity and diffusion coefficient based on the Einstein's law (Andrade, 1993), and some methods of converting the electric resistivity into the diffusion coefficient of chloride ion were variously proposed (Sengul and Gjrrv, 2008; Andrade, 2005; McCarter et al., 2000; Shi et al., 1999; Streicher et al., 1995; Garboczi, 1990 and many others). In addition to this, a method based in the use of a Non Destructive Test as electric resistivity to predict the service life of concrete structures was proposed (Andrade et al., 2010). Moreover, AASHTO Designation: TP 95-11 can be mentioned as an example of the quality control method on durability. AASHTO specifies the judgement method of

concrete ability concerning with the resistance to the penetration chloride ion using electric resistivity as AASHTO Designation: TP 95-11, Standard Method of Test for Surface Resistivity Indication of Concrete's Ability to Resist Chloride Ion Penetration.

Actually, a good correlation was observed between the electric resistivity of which the inner condition was enough wet and the apparent diffusion coefficient of chloride ion from fields values in several previous studies (Presuel-Moreno et al., 2010). However, the electric resistivity measured on site is affected by temperature, moisture and ion concentrations in concrete (Presuel-Moreno et al., 2010; Saleem, 1996). In addition, concerning moisture, it was pointed out that the inner gradient of water content in concrete affected the measuring results of the electric resistivity (Gowers and Millard, 1999). Accordingly, it is necessary to consider the effects of these factors when estimating the diffusion coefficient of chloride ion from the resistivity measured on site.

**Purpose.** The purpose of this study is to evaluate the variation of the diffusion coefficient of chloride ion estimated by the electric resistivity. The concrete specimens were exposed in tidal zone. Here, the electric resistivity was obtained by the four probes method (Wenner technique) on site. Consequently, the estimation results of the diffusion coefficient of chloride ion were affected by the variation of the electric resistivity due to several factors described above. In this study, the variation of the electric resistivity was also discussed.

### Fabrication of specimens

The Results obtained from two types of specimens will be discussed in this study in order to lead to a more general conclusion. The shape of the type-A specimens was a cuboid, and the size was 1000x1000x300 mm. In the type-A specimens, the deformed steel bars D13 were placed at the cover depth of 70 mm. On the other hands, the size of the type-B specimens was 150x270x150 mm. There was no steel bar in the type-B specimens. Table 1 shows the number of the specimens and curing conditions. The exposure surface was 1000x1000 mm and 150x270 mm respectively Type-A and Type-B.

**Table 1. Number of the Specimens, Curing Conditions and Exposure Conditions**

Type	Number	Cement	W/B	Curing Conditions	Exposure Conditions
A	HPC39-AET	HPC	0.39	1 day demolding and atmospheric curing for 27 days	Exposed an actual tidal zone during 21 months. The average yearly temperature was 16.6 °C.
A	BB37-AET	BB	0.37		
B	HPC36	HPC	0.36	1 day demolding and underwater curing for 27 days	Wet-dry cyclic test in laboratory. Wet condition was under 10 % NaCl solution during 4 days and the dry condition was in R. H. (50 ± 10) % during 3 days. Cyclic count was 16 times. Air temperature was set to 20 ± 2 °C.
B	FA35	FA	0.35		
B	OPC35	OPC	0.55		
B	OPC55	OPC	0.55		
B	OPC65	OPC	0.65		
B	OPC55-d1	OPC	0.55	1 day demolding and atmospheric curing for 27 days	
B	OPC55-d5	OPC	0.55	24 h demolding and atmospheric curing for 27 days	

HPC: High early strength cement, BB: Portland blast furnace cement type B, OPC: Ordinary Portland cement, FA: Fly ash of which the replacement ratio was 20 % of OPC.

## Measuring Items

**Electric resistivity.** The electric resistivity of the specimens was measured by the four probes methods (Wenner method). The alternating voltage and the frequency impressed to the specimen were 30 V and 73.3 Hz, respectively. The distance between the electrodes was set to 2, 3, 4, 5 cm. The electric resistivity can be calculated by using Equation (1).

$$\rho = 2\pi a \cdot V/I \quad (1)$$

where  $V$  is the potential difference between potential difference electrode (V),  $I$  is the current value flowing through the specimen (A),  $a$  is the probe spacing (m).

**Relative water content ratio.** The core samples obtained from the specimens by using a dry-type boring machine were cut into slices with a thickness of about 1 cm by a dry-type diamond cutter. The weight of the slice samples were measured after adjusting the moisture state. The relative water content ratio was calculated by Equation (2).

$$w = \frac{(W_w - W_d) - (W_w - W_i)}{(W_w - W_d)} \quad (2)$$

where  $w$  is the relative water content ratio,  $W_d$  is the weight of a slice sample of the absolute dry condition (g),  $W_i$ : the weight of a slice sample immediately after cutting (g),  $W_w$  is the weight of a slice sample of the saturated conditions.

**Apparent  $\text{Cl}^-$  diffusion coefficient.** Apparent  $\text{Cl}^-$  diffusion coefficient was evaluated in accordance with JSCE-G572 (Japan Society of Civil Engineers, 2003).

**Estimation  $\text{Cl}^-$  diffusion coefficient.** Estimation  $\text{Cl}^-$  diffusion coefficient,  $D_{Cl}$  was evaluated in accordance with the previous study (Minagawa et al., 2010).  $D_{Cl}$  can be calculated by Equation (3).  $D_{Cl}$  is a type of effective diffusion coefficient.

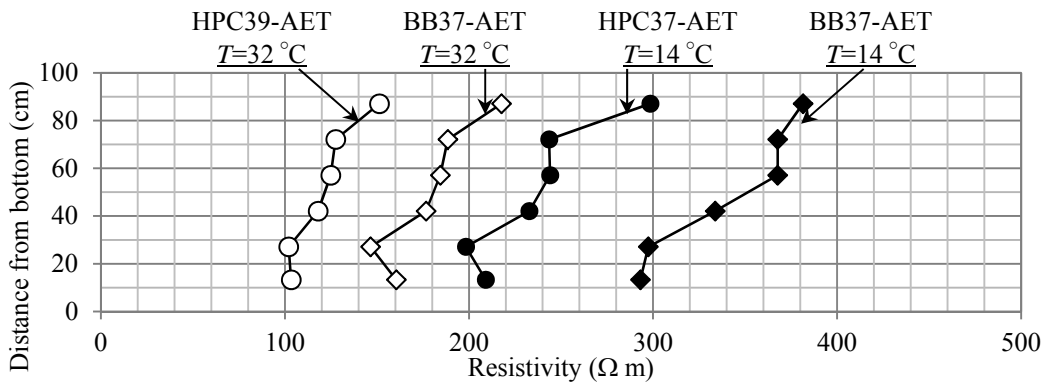
$$D_{Cl} = \frac{1}{\rho} \cdot \frac{k \cdot T \cdot \left( 1 - \ln 10 \times C_{Cl} \cdot \frac{0.51 \cdot Z_{Cl}^4}{4 \sqrt{T} \cdot (1 + \sqrt{T})^2} \right) \cdot B_{Cl}}{F \cdot e \cdot \sum_n (Z_n^2 \cdot B_n \cdot C_n)} \quad (3)$$

where is the estimation  $\text{Cl}^-$  diffusion coefficient,  $\rho$  is the electric resistivity ( $\Omega$  m),  $k$  is the Boltzman number ( $=1.38 \times 10^{-23}$  J/K),  $T$  is temperature (K),  $F$  is the Faraday constant ( $=9,650,000$  C/mol),  $n$  is the ionic species,  $Z$  is the ionic charge number,  $B$  is absolute mobility ( $\text{m N}^{-1} \text{s}^{-1}$ ),  $C$  is the concentration of ions ( $\text{mol/m}^3$ ),  $e$  is the elementary charge ( $=1.60 \times 10^{-19}$  C).

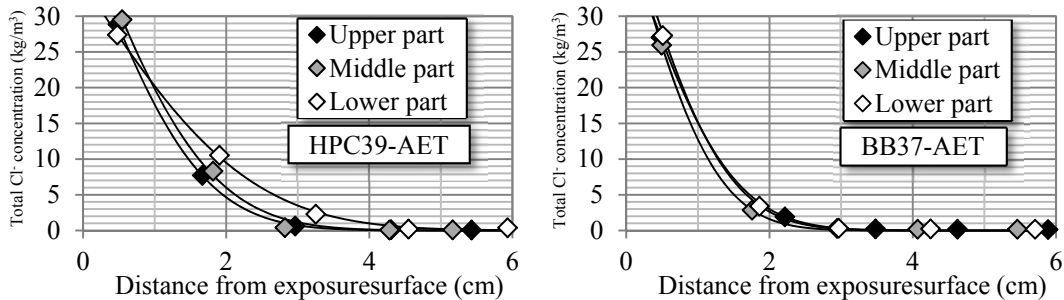
## Results and Discussions

**Temperature, moisture and ion concentration dependency of electric resistivity.** Figure 1 shows the measuring results of the electric resistivity obtained from the type-A specimens. The resistivity in Figure 1 measured at spring and summer season, because it was desirable to acquire the data in temperature almost equivalent to average yearly temperature, or different temperature. It is obvious that the electric resistivity of concrete becomes lower due to increase in air temperature. Thus, when there is a marked difference between the temperatures of the measuring time and the average yearly temperature, it is necessary to make an appropriate correction for the electric resistivity due to the temperature difference.

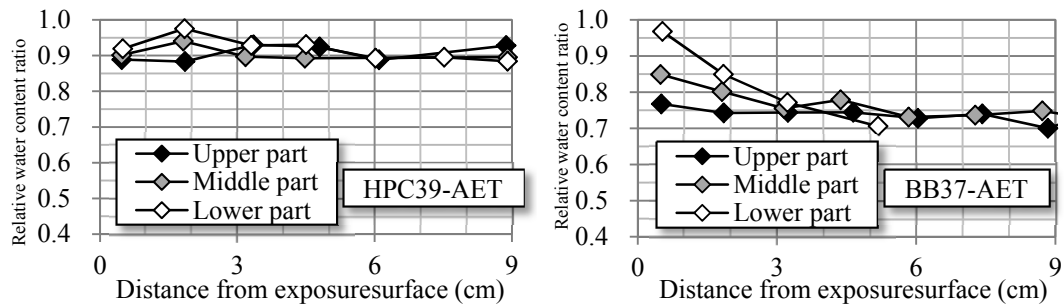
In addition to this, it was observed that the electric resistivity tends to decrease as the lower position of the specimens. The reasons of this tendency can be explained on the basis of the relative water content ratio and ion concentration in concrete. Figure 2 shows the measuring results of the relative water content ratio in the type-A specimens. In the specimen of BB37-AET, the relative water content ratio around the surface of the specimen increases as the lower position. On the other hand, the relative water content in the specimen of HPC39-AET is almost the same value regardless of the position. Here, Figure 3 shows the chloride ion concentration in the specimen of HPC39-AET tends to increase as the lower position. The electric resistivity of concrete becomes lower with increasing ion concentration and moisture content in concrete (Saleem, 1996). Hence, this spatial variation of the electric resistivity in the specimens is attributed to a distribution of the ion concentration and the relative water content ratio in concrete. This fact suggests the need of an appropriate correction for the electric resistivity due to the ion concentration and moisture content in concrete if it is necessary to estimate the diffusion coefficient from electric resistivity strictly.



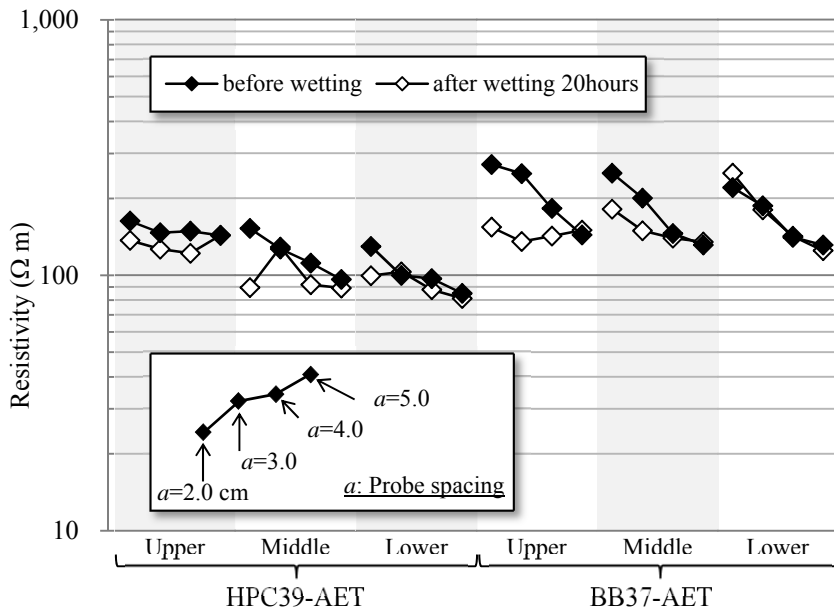
**Figure 1. The measuring results of the electric resistivity obtained from the type-A specimens using the distance of electrodes  $a=4$  cm.**



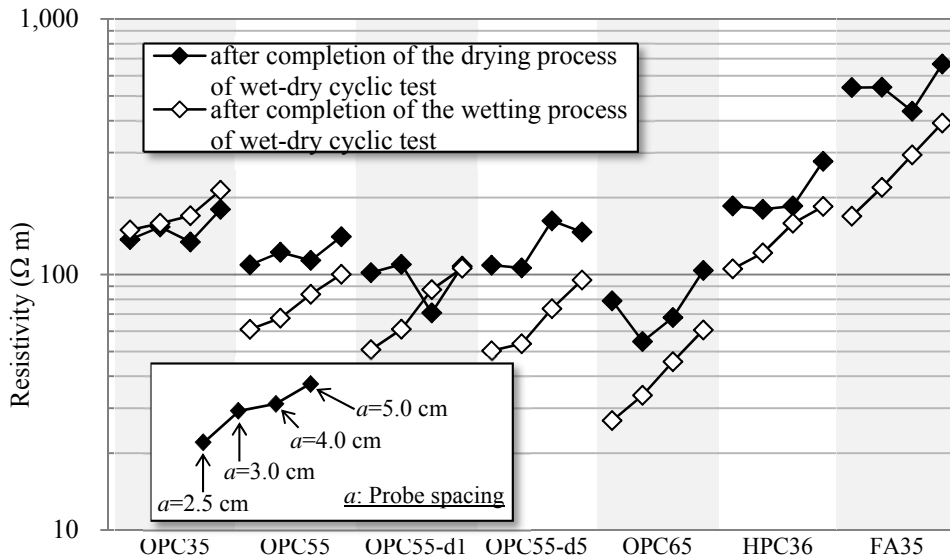
**Figure 2. The relative water content ratio in the type-A specimens**



**Figure 3. The chloride ion concentration in the type-A specimens**



**Figure 4. The probe spacing  $a$  dependency of the measuring electric resistivity (type-A specimens)**



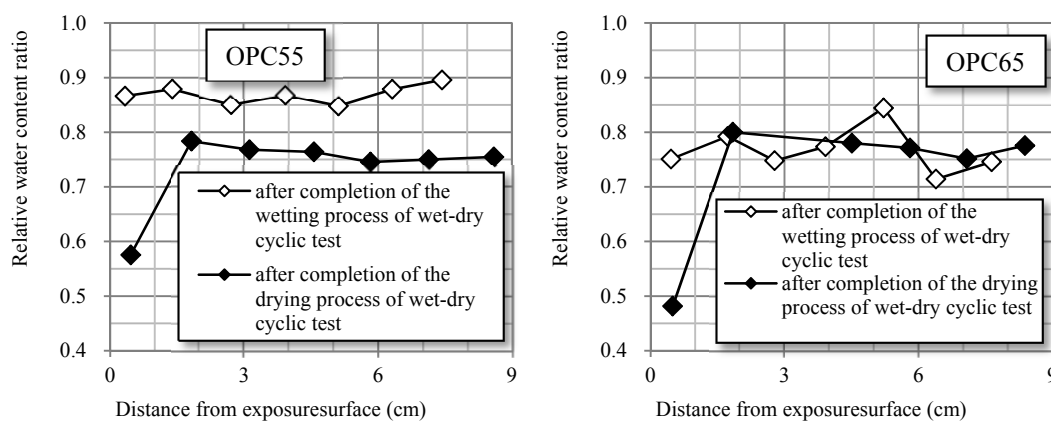
**Figure 5. The probe spacing  $a$  dependency of the measuring electric resistivity (type-B specimens)**

**Probe spacing dependency of electric resistivity.** Figure 4 and Figure 5 shows the probe spacing dependency of the measuring electric resistivity obtained from the specimens of type-A and type-B, respectively. From these figures, it is obvious that the probe spacing dependency is different between the specimen of type-A and type-B.

In the specimens of type-A, the measuring electric resistivity decreases with increasing the probe spacing. The electric resistivity at the around surface is expected to be lower than or equal to the deep region. Hence, the probe spacing dependency observed on the specimens of type-A is not caused by the distribution of the ion concentration or moisture content, because the electric resistivity would increase with increasing the probe spacing if these factors had effected on the measuring electric resistivity. Here, it is expected that the probe spacing dependency observed on the specimens of type-A is attributed to the presence of the steel bar rather than the specimen size, in view of the influence of steel bars and specimen size on the measuring electric resistivity as shown by Gowers and Millard (1999).

On the other hand, in the specimens of type-B, the measuring electric resistivity evaluated after completion of the wetting process of wet-dry cyclic test increases with increasing the probe spacing. The specimens size of type-B is smaller than type-A. Consequently, the measuring electric resistivity of the type-B specimens becomes susceptible to the geometric relationship between the probe spacing and the specimen size. Gowers and Millard (1999) show the measuring electric resistivity increases as the probe spacing increases, if the ratio of the specimen size to the probe spacing becomes smaller. In addition, the measuring electric resistivity evaluated after completion of the drying process of wet-dry cyclic test tends to reach a minimum value at the probe spacing  $a=3$  cm or 4 cm. This is because the electric resistivity at the around surface is higher than the deep region due to the low relative water content near the surface (see Figure 6). It is expected that the interaction of the smaller specimen size and the lower relative water content near the surface make the minimum value of the measuring electric resistivity.

From these results, the presence of steel bar in concrete, the geometric relationship between probe spacing and specimen size, the depth direction distribution of the moisture content in concrete provide the variation of the measuring electric resistivity obtained by the different probe spacing. Moreover, if these factors are conflict, the measuring value of the electric resistivity obtained by some probe spacing might have extreme values.

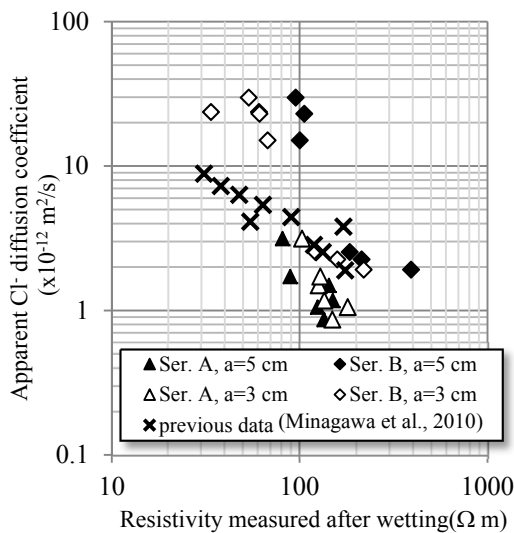


**Figure 6. The relative water content ratio in the type-B specimens**

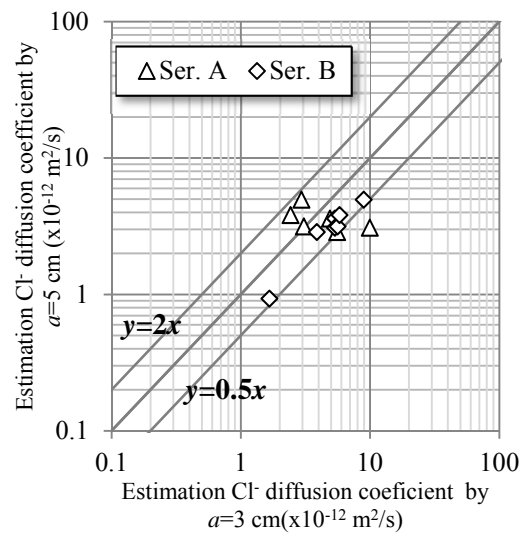
**Relationship between apparent  $\text{Cl}^-$  diffusion coefficient, electric resistivity and estimation  $\text{Cl}^-$  diffusion coefficient.** Figure 7 shows the relationship between the apparent  $\text{Cl}^-$  diffusion coefficient and the measuring electric resistivity. On the other hand, Figure 8 shows the comparison results of the estimation  $\text{Cl}^-$  diffusion coefficient obtained from different probe spacing  $a=3\text{cm}$  and  $5\text{cm}$ . Here, the electric resistivity was measured after wetting treatment for 20 hours or the completion of the wetting process of wet-dry cyclic test. Because the electric resistivity measured after wetting treatment tends to have a good correlation to apparent  $\text{Cl}^-$  diffusion coefficient (Plesuel-Moreno, 2010).

Figure 7 indicates that a strict estimation of apparent  $\text{Cl}^-$  diffusion coefficient requires an appropriate correlation of the measuring electric resistivity due to the several factors described above. However, the difference of the estimation  $\text{Cl}^-$  diffusion coefficients obtained by the probe spacing of  $a=3\text{cm}$  and  $5\text{cm}$  is from 0.5 to 2.0 times as shown in Figure 8. Therefore, it is possible to use for the discovery and quantitative evaluation of significant defect related to chloride ion penetration through concrete.

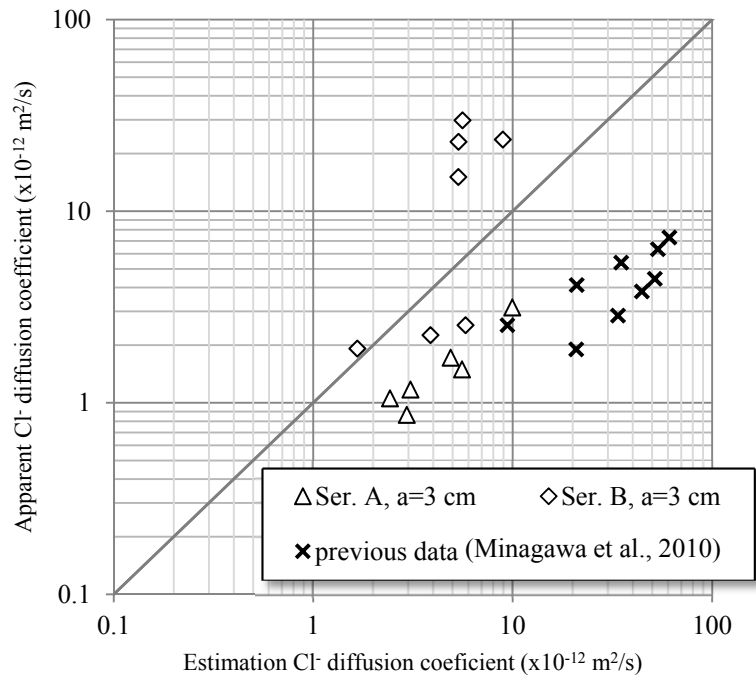
Figure 9 shows the comparison results of the apparent  $\text{Cl}^-$  diffusion coefficient and the estimation  $\text{Cl}^-$  diffusion coefficient obtained by the probe spacing  $a=3\text{cm}$  and after wetting. In most of the data, the estimation  $\text{Cl}^-$  diffusion coefficient is higher than the apparent  $\text{Cl}^-$  diffusion coefficient. This result is attributed to the reacting or binding of  $\text{Cl}^-$  into cement hydrates. However, this relationship is not absolute and can be inverted in the case of the porous specimens due to its high water cement ratio. The apparent  $\text{Cl}^-$  diffusion coefficient of these specimens is over  $10 \times 10^{-12} \text{ m}^2/\text{s}$ . This tendency is expected to be caused by advection mechanism. Thus, if the spatial variation of diffusion coefficient of such relatively porous concrete is evaluated by using the electric resistivity, it is important to consider the effect of advection on the chloride penetration.



**Figure 7. Relationship between apparent  $\text{Cl}^-$  diffusion coefficient and electric resistivity after wetting**



**Figure 8. Comparison results of estimation  $\text{Cl}^-$  diffusion coefficient obtained from different probe spacing  $a=3\text{cm}$  and  $5\text{cm}$**



**Figure 9. Comparison results of apparent Cl<sup>-</sup> diffusion coefficient and estimation Cl<sup>-</sup> diffusion coefficient obtained by the probe spacing  $a=3\text{cm}$  and after wetting**

## CONCLUSIONS

The on-site measuring electric resistivity of the concrete exposed at tidal zone is influence of temperature, moisture and ion concentration as well as the presence of steel bar in concrete and the geometric relationship between probe spacing and specimen size. Moreover, if these factors are conflict, the measuring value of the electric resistivity obtained by some probe spacing might have extreme values.

The difference of the estimation Cl<sup>-</sup> diffusion coefficients obtained by the probe spacing of  $a=3\text{ cm}$  and  $5\text{ cm}$  is from 0.5 to 2.0 times. Therefore, it is possible to use for the discovery and quantitative evaluation of significant defect related to chloride ion penetration through concrete.

If the spatial variation of diffusion coefficient of such relatively porous concrete is evaluated by using the electric resistivity, it is important to consider the effect of advection on the chloride penetration.

## REFERENCES

- Andrade, C. (1993). "Calculation of chloride diffusion coefficients in concrete from ionic measurement." *Cement and Concrete Research*, 23, 724-742.
- Andrade, C. (2005). "Model for Prediction of Reinforced Concrete Service Life Based on Electrical Resistivity." *IBRACON Materials Journal*, 1(1), 61-65.
- Andrade, C. and d'Andrea R. (2010). "The Use of Electrical Resistivity as a NDT for the Specification of Concrete Durability." *Proceedings of the 6th International*



- Conference on Concrete under Severe Conditions: Environment and Loading*, 195-200.
- BRE Digests 434 (1998). "Corrosion of reinforcement in concrete: electrochemical monitoring".
- Japan Society of Civil Engineers (2003), "JSCE Standards on Test Method for Diffusion Coefficient of Chloride Ion in Concrete." *JSCE Guidelines for Concrete*, 2.
- Garboczi, J., E. (1990). "Permeability, Diffusivity, and Microstructural Parameters: A Critical Review." *Cement and Concrete Research*, 20(5), 591-601.
- Gowers, K. R. and Millard, S. G. (1999). "Measurement of Concrete Resistivity for Assessment of Corrosion Severity of Steel Using Wenner Technique." *ACI Materials Journal*, September-October, 536-541.
- McCarter, J., M., Starrs, G., Chrisp, T., M. (2000). "Electrical conductivity, diffusion, and permeability of Portland cement-based mortars." *Cement and Concrete Research*, 30, 1395-1400.
- Minagawa, H., Hisada, M. and Ehara, A. (2010). "Relationship between electric resistivity and diffusion coefficient of chloride ion in mortar" *Proceedings of the 6th International Conference on Concrete under Severe Conditions: Environment and Loading*, 641-649.
- Plesuel-Moreno, F. J., Suarez, A., Lasa, I., Paredes, M. (2010). "Surface resistivity profiles on marine substructures to assess concrete permeability." *Proceedings of the 6th International Conference on Concrete under Severe Conditions: Environment and Loading*, 227-235.
- Polder, R. et al. (2000). "RILEM TC 154-EMC: Electrochemical techniques for measuring metallic corrosion, Test methods for on site measurement of resistivity of concrete", *Materials and Structures*, 33, 603-611.
- Saleem, M., Shameem, M., Hussain, S. E. and Maslehuddin, M. (1996). "Effect of moisture, chloride and sulphate contamination on the electrical resistivity of Portland cement concrete" *Construction and Building Materials*, 10(3), 209-214.
- Sengul, O., Gjørsv, E. O. (2008). "Electrical Resistivity Measurements for Quality Control during Concrete Construction." *ACI materials Journal*, 105(6), 541-547.
- Shi, M., Chen, A. and Sun, J. (1999). "Determination of chloride diffusivity in concrete by AC impedance spectroscopy." *Cement and Concrete Research*, 29(7), 1111-1115.
- Streicher, P. E. and Alexander, M. G. (1995). "A chloride Conduction Test for Concrete." *Cement and Concrete Research*, 25(6), 1284-1294.