# Non-Steady-State Chloride Migration Test on Mortar with Supplementary Cementitious Materials

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## ABSTRACT

The non-steady-state migration test for measuring the chloride migration coefficient was performed on mortar specimens fabricated with supplementary cementitious materials. A careful examination of the test results revealed that the use of more than one specimen with different test durations is recommended for obtaining reliable chloride migration coefficients. Additionally, the voltage applied to the specimens should be set at values that prevent a substantial increase in electrical current and solution temperature during the test. The chloride migration coefficients derived from the non-steady-state migration test were subsequently compared with the chloride diffusion coefficients obtained from the immersion test. Although there were discrepancies between the values of these two coefficients, both test results indicated that the mixing of supplementary cementitious materials contributed to the improved resistance of mortar to chloride ingress.

**Keywords.** Non-Steady-State Migration Test, Chloride Migration Coefficient, Immersion Test, Chloride Diffusion Coefficient, Supplementary Cementitious Materials

## INTRODUCTION

There are several types of laboratory tests for investigating the resistance of concrete to chloride ingress. The non-steady-state migration test is globally recognized as a simple, precise, and reliable method according to interlaboratory comparisons (Tang, et al., 2012). The non-steady-state migration test for measuring the chloride migration coefficient of concrete, mortar, and cement-based repair materials has been standardized as NT BUILD 492 in Nordic countries (Nordtest, 1999). However, the testing procedure of the non-steady-state migration test has not yet been critically reviewed.

Chloride ingress in concrete is a complex phenomenon, and the resistance of concrete to this problem is affected by many factors, such as binder type, curing period, and concrete age. This implies that these factors also have a substantial effect on the laboratory test results. Thus, a reliable laboratory test is required to deliver test results that reflect the effects of those factors.

The purpose of the experimental program described in this paper was to investigate an appropriate testing procedure for the non-steady-state migration test. To achieve this goal, the non-steady-state migration test was performed on mortar specimens fabricated with supplementary cementitious materials (SCMs). The chloride migration coefficients derived from the non-steady-state migration test were subsequently compared with the chloride diffusion coefficients obtained from the immersion test.

## EXPERIMENTAL PROGRAM

**Mortar Specimens.** Three types of mortar specimens (OPC100, SG50, and FA20) were used in this experimental program. The specimens were fabricated by using three different binders: (1) ordinary Portland cement (OPC); (2) ground granulated blast-furnace slag (GGBFS); and (3) fly ash (FA). The mix proportion and the fresh and strength properties are shown in **Table 1** and **Table 2**, respectively.

### Table 1.  Mix Proportions

| ID | Binder Composition | Water / Binder Ratio | Sand / Binder Ratio | Content (kg/m$^3$) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Water | Cement | GGBFS | FA | Sand |
| OPC100 | OPC (100%) | | | 237 | 592 | - | - | 1480 |
| SG50 | OPC (50%), GGBFS (50%) | 0.4 | 2.5 | 235 | 293 | 293 | - | 1467 |
| FA20 | OPC (80%), FA (20%) | | | 234 | 468 | - | 117 | 1461 |

Note: Ordinary Portland cement (OPC, 3.16 g/cm$^3$); ground granulated blast-furnace slag (GGBFS, 4210 cm$^2$/g, 2.88 g/cm$^3$); fly ash (FA, 4140 cm$^2$/g, 2.35 g/cm$^3$)

### Table 2.  Fresh and Strength Properties

| ID | Mortar Flow (mm) | Air Content (%) | Compressive Strength (N/mm$^2$) | |
|---|---|---|---|---|
| | | | 28 days | 91 days |
| OPC100 | 109 × 110 | 7.2 | 76.0 | 87.2 |
| SG50 | 112 × 112 | 7.7 | 59.4 | 81.3 |
| FA20 | 119 × 120 | 6.7 | 67.0 | 80.0 |

Note: The mortar flow and air content were measured immediately after mixing the mortar. The compressive strength was measured using three cylinders (φ50×100 mm) for each mix at the age of 28 and 91 days.

The specimens were used for the non-steady-state migration test and immersion test after curing in water until the age of 28 or 91 days. The experimental procedures for each test method are described in the following section.

**Non-Steady-State Migration Test.**  The non-steady-state migration test has been adopted in NT BUILD 492 and AASHTO TP 64 (AASHTO, 2007). In NT BUILD 492, the chloride migration coefficient is computed, while in AASHTO TP 64, the chloride penetration rate is used to evaluate the resistance of concrete to chloride ingress. In Japan, we are also working to develop a standard test method for deriving the chloride migration coefficient from the non-steady-state migration approach.

To implement a critical review of the testing procedure adopted in the existing non-steady-state migration tests, the investigation focused on the effects of the following three parameters: (1) applied voltage; (2) test duration; and (3) pretest water curing period. The experimental parameters are summarized in **Table 3**. For the specimens cured in water until the age of 28 days, two levels of voltage were applied for seven different test durations, and for those cured in water until the age of 91 days, three levels of voltage were applied for five different test durations. This procedure is different from that adopted in the existing non-

steady-state migration tests. For instance, the applied voltage is adjusted in accordance with the initial electrical current measured at the applied voltage of 30 V in NT BUILD 492 and 60 V in AASHTO TP 64, respectively. Moreover, the test duration in NT BUILD 492 is 24 h for most cases, and that in AASHTO TP 64 is fixed at 18 h. This implies that only one test duration is set in the existing non-steady-state migration tests. Once again, it should be emphasized that the experimental program described herein employed several variations of applied voltage, test duration, and pretest water curing period, and aimed to clarify the effects of these parameters on the test results.

**Table 3.  Experimental Parameters of Non-Steady-State Migration Test**

| Applied Voltage (V) | Test Duration (hours) | Water Curing Period (days) |
|---|---|---|
| 30, 45 | 3 to 30 (7 variations) | 28 |
| 15, 30, 45 | 3 to 45 (5 variations) | 91 |

Note: The test duration was determined so that chloride in the catholyte solution would not penetrate the specimen and reach the anolyte solution.

The specimens used for the non-steady-state migration test were fabricated by casting mortar in plastic forms ($\varphi 100 \times 100$ mm). The specimens were cured in water at a temperature of 20°C from the day after casting to the age of 28 or 91 days. After the water curing procedure, a 50-mm-thick slice was cut from the center of each specimen. The side surface of the slice was sealed with epoxy resin to prevent chloride migration from other than an exposed surface. Then, the slice was placed in a desiccator, depressurized with a vacuum pump, saturated with deionized water, and kept still for more than 24 h.

The saturated specimen was installed in the same apparatus as that described in AASHTO T 277 (AASHTO, 2007) and ACTM C 1202 (ASTM, 2010). A 10% NaCl solution was used as the catholyte solution, and a 0.3 mol/l NaOH solution was used as the anolyte solution. After two reservoirs were filled with the solutions, the predetermined voltage was applied to the specimen using the DC power supply in the laboratory at a room temperature of 20°C. The electrical current passing through the specimen and the temperature of the catholyte solution were measured during the test. When the test duration ended, the DC power supply was turned off and the specimen was removed from the apparatus. The removed specimen was split axially, and a 0.1 mol/l silver nitrate solution was sprayed on the split surface. When the white silver chloride was clearly visible on the split surface, the chloride penetration depth was measured at nine equally spaced points. The apparatus, experimental setup, and test specimen are shown in **Figure 1**.



**Figure 1.  Apparatus, Experimental Setup, and Test Specimen**

Based on the measured chloride penetration depth, the chloride migration coefficient derived from the non-steady-state migration test was computed by adopting two approaches. One approach is based on the original equation in NT BUILD 492. In this experimental program,

the definitions of the variables in the original equation were slightly modified to make this equation applicable to the specimens with SCMs and to obtain more precise chloride migration coefficients. According to this approach, the chloride migration coefficient based on the original equation in NT BUILD 492, $D_{nssm,NT}$, is given by:

$$D_{nssm,NT} = \frac{RTL}{zFE} \cdot \frac{x_d - \alpha\sqrt{x_d}}{t}$$

(1)

where

$$\alpha = 2\sqrt{\frac{RT}{zFE}} \cdot erf^{-1}\left(1 - \frac{2c_d}{c_0}\right)$$

(2)

$D_{nssm,NT}$: chloride migration coefficient based on the original equation in NT BUILD 492 ($m^2$/s); $z$: absolute value of the ion valance for chloride, 1 (kg/$m^3$); $F$: Faraday constant, $9.648\times10^4$ (J/(V·mol)); $E$: average value of the initial and final applied voltages measured between two solutions (V); $R$: gas constant, 8.314 (J/(K·mol)); $T$: average value of the temperature in the catholyte solution during the test (K); $L$: thickness of the specimen (m); $x_d$: average value of the chloride penetration depth (m); $t$: test duration, (s); $c_d$: chloride concentration at which the color changes, assuming 0.07 mol/l for all cases; $c_0$: chloride concentration in the catholyte solution, assuming 2 mol/l.

Due to the benefit of using more than one specimen with different test durations, we proposed a further modification of Equation (1). Namely, we introduced the chloride penetration rate factor, $K$, which was determined as the slope of the regression line between the test duration, $t$, and the average value of the chloride penetration depth, $x_d$. This modification is based on two reasons. The first reason is to avoid measurement errors due to variations in the chloride penetration depth, especially for the specimens mixed with SCMs, since the mixing of a high volume of GGBFS is likely to result in an unclear color change of the white silver chloride. Additionally, the chloride concentration at the color change of the white silver chloride was reported to vary depending on the mix proportion (Baroghel-Bouny, 2007a, 2007b). The second reason is that the rate of chloride migration may change during the test since various chemical reactions are induced in the migration process. In accordance with this approach, the chloride migration coefficient based on the PWRI recommendation, $D_{nssm,PWRI}$, is given by:

$$D_{nssm,PWRI} = \frac{RTL}{zFE} \cdot K$$

(3)

where

$D_{nssm,PWRI}$: chloride migration coefficient based on the PWRI recommendation ($m^2$/s), $K$: chloride penetration rate factor (m/s).

In a later section of this paper, the chloride migration coefficients based on these two approaches are compared by using the test results obtained in this experimental program.


**Immersion Test.** The immersion test has been standardized in Japan, North America, and Europe. Although the existing standard tests employ similar testing procedures, there are several discrepancies among the testing procedures developed in different regions. One of the most noticeable discrepancies is the concentration of NaCl solution used to immerse the

specimens. While the test method established by the Japan Society of Civil Engineers uses a 10% NaCl solution (JSCE, 2005), those adopted in North America and Europe employ concentrations other than 10%. For instance, a 3% NaCl solution is used in the ponding tests of ASTM C 1543 (ASTM, 2010) and AASHTO T 259 (AASHTO, 2006), and a solution containing 165 g NaCl per liter is employed in the immersion tests of ASTM C 1556 (ASTM, 2004) and NT BUILD 443 (Nordtest, 1995). In this experimental program, salt solutions with three NaCl concentrations (3%, 10%, and 20%) were used to investigate the effects of the difference in NaCl concentration on the test results.

The fabrication of specimens prepared for the immersion test was based on the JSCE test method. Cylinders (φ100×200 mm) were cured in water at a temperature of 20°C from the day after casting to the age of 28 days. After the water curing procedure, the cylinders were shaped into 150-mm-thick cylinders by cutting off a 25-mm-thick disk from both the top and bottom ends. The bottom and side surfaces of the shaped cylinders were sealed with epoxy resin to prevent chloride ingress. The sealed cylinders were immersed in the NaCl solutions. After a 6-month immersion period, the cylinders were sliced into 10-mm-thick disks from the top surface, and the chloride content of each disk was measured to obtain the chloride profiles.

The chloride diffusion coefficient derived from the immersion test, $D_{nss}$, is determined by curve-fitting the chloride profile to the following equation, which is one of the solutions to Fick's second law:

$$C(x,t) - C_i = (C_o - C_i)\left\{1 - erf\left(\frac{x}{2\sqrt{D_{nss}t}}\right)\right\}$$

(4)

where

$C(x,t)$: chloride content (kg/m$^3$) measured at depth $x$ (m) and time $t$ (s); $C_i$: initial total chloride content (kg/m$^3$); $C_o$: total chloride content at the surface (kg/m$^3$); $x$: depth (m); $D_{nss}$: chloride diffusion coefficient (m$^2$/s); $t$: immersion time (s).

## TEST RESULTS

**Depth and Rate of Chloride Penetration.** The chloride penetration depth measured on the specimens tested after the 91-day water curing procedure is shown in **Figure 2**. The regression lines for the data obtained with the same applied voltage are also included in the figure. It can be seen that the chloride penetration depth is proportional to the test duration in all cases. It is, however, interesting to observe that the intercepts of all regression lines are positive. This fact indicates that the chloride penetration rate decreased during the test although chloride migrated further into the specimens with an increase in the test duration.

In order to investigate variations in the chloride penetration rate during the test, the chloride penetration rate obtained in the specimens with applied voltage of 30 V is presented in **Figure 3**. The chloride penetration rate is computed by dividing the chloride penetration depth by the test duration. The K factor, which is defined as the slope of the regression line in the PWRI recommendation, is also provided in the figure. As expected, the chloride penetration rate decreased with an increase in the test duration in all cases. Although the chloride penetration rate for SG50 and FA20 remained at the same level after 15 h, that for OPC100 continued to decrease from 15 to 30 h. Additionally, it should be stressed that the chloride penetration rate of SG50 and FA20 after 15 h and of OPC100 at 30 h were almost

equal to the K factor. Thus, it is reasonable to consider that the chloride penetration rate decreased to a specific value with an increase in the test duration and that this specific value can be predicted by using the K factor. Moreover, these findings suggest that when a test is conducted using specimens with only one test duration and this test duration is too short to obtain a stable chloride penetration rate, the test is likely to result in an overestimation of the chloride penetration rate.
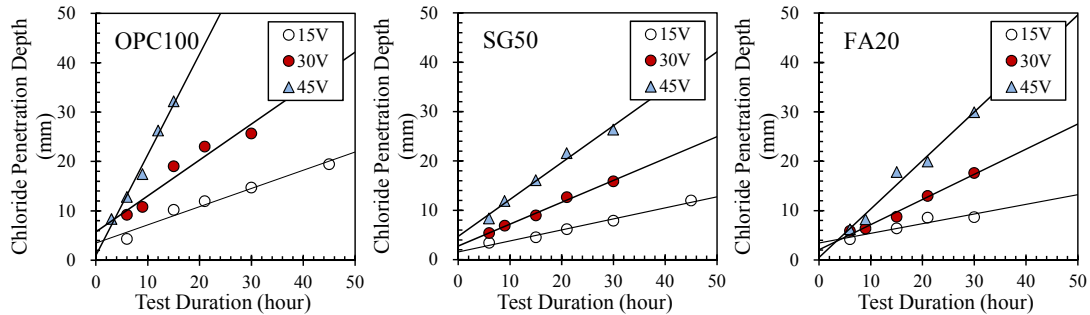


**Figure 2. Chloride Penetration Depth**
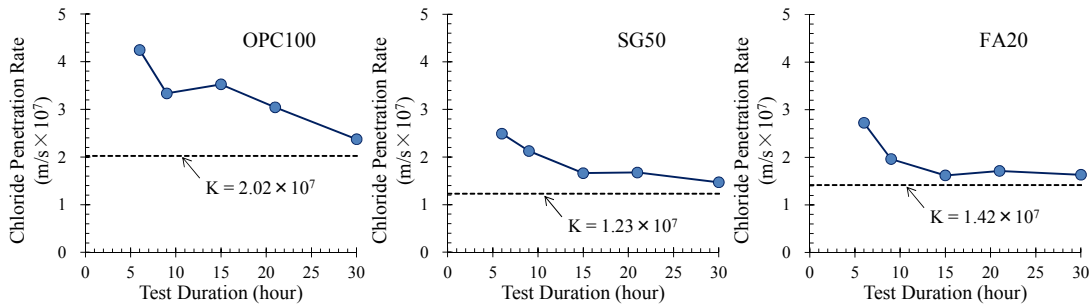


**Figure 3. Chloride Penetration Rate and K Factor**

**Chloride Migration Coefficient.**   The chloride migration coefficients based on the original equation in NT BUILD 492, $D_{nssm,NT}$, and the PWRI recommendation, $D_{nssm,PWRI}$, are presented in **Figure 4**. The two chloride migration coefficients in **Figure 4** have quite similar distributions to the chloride penetration rate in **Figure 3**. Namely, the chloride migration coefficient is substantially influenced by the chloride migration rate. $D_{nssm,NT}$ of SG50 and FA20 decreased with an increase in the test duration before 15 h and remained at almost the same level after 15 h. Additionally, it should be noted that the final values of $D_{nssm,NT}$ for SG50 and FA20 were nearly equal to those of $D_{nssm,PWRI}$. Meanwhile, $D_{nssm,NT}$ of OPC100 decreased from 15 to 30 h and was almost equal to $D_{nssm,PWRI}$ at 30 h. These facts indicate that a test with only one test duration, which is not long enough to obtain a stable chloride migration rate, is likely to overestimate the chloride migration coefficient. Based on these findings, the use of more than one specimen with different test durations is recommended for obtaining reliable chloride migration coefficients.

The chloride migration coefficients based on the PWRI recommendation are summarized in **Figure 5**. Comparing the chloride migration coefficients obtained by using the same applied voltage, the chloride migration coefficients provided in the specimens after the 91-day water curing procedure are lower than those estimated in the specimens after the 28-day water curing procedure in all binder types. This trend is especially seen in the FA20 specimen. It is reasonable to assume that this decrease was achieved by extending the pretest water curing period. Thus, the chloride migration coefficient derived from the non-steady-state migration

test is considered an appropriate indicator for evaluating the effects of the binder type and pretest water curing period on the resistance to chloride ingress.

On the other hand, when comparing the chloride migration coefficients provided in the specimens with the same water curing period, those with the applied voltage of 45 V are larger than in the other cases. This fact implies that the use of a higher applied voltage may provide overly large chloride migration coefficients. The mechanism of this problem is investigated in the following section by focusing on the electrical current and solution temperature measured during the test.
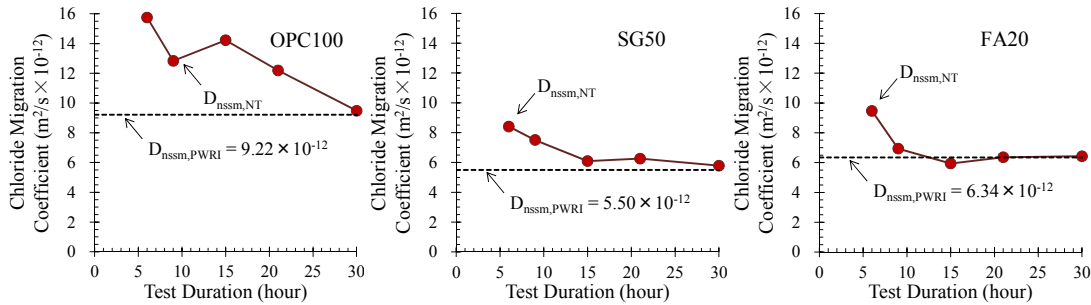
**Figure 4.  Comparison of Chloride Migration Coefficients**
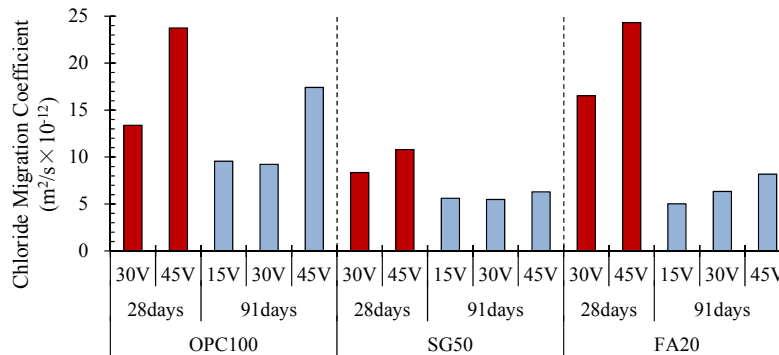
**Figure 5.  Chloride Migration Coefficient Based on PWRI Recommendation**
Note: The chloride migration coefficients are presented for each binder type, pretest water curing period, and applied voltage.

**Electrical Current and Solution Temperature.** The electrical current and temperature in the catholyte solution during the test are shown in **Figure 6** and **Figure 7**, respectively. This data was measured in specimens tested after the 91-day water curing procedure. According to these two figures, the initial values of the electrical current were roughly proportional to the applied voltage and those of the temperature in the catholyte solution were nearly equal to 20°C in all cases. The electrical current and the temperature in the catholyte solution, however, increased significantly during the test when the applied voltage was set to 45 V. Additionally, this increase was observed almost simultaneously. It is important to note that the increase in the electrical current leads directly to an increase in the chloride migration rate since the chloride migrates into the specimen with electrical current in this test method. Namely, the large chloride migration coefficients in the specimens with applied voltage of 45 V resulted from overly rapid chloride migration due to the high applied voltage. Accordingly, it is recommended that the applied voltage be set at a value that prevents a substantial increase in the electrical current and solution temperature during the test.
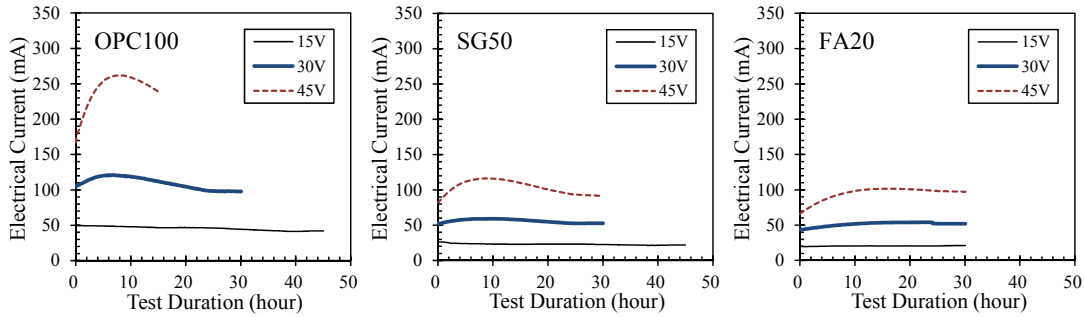
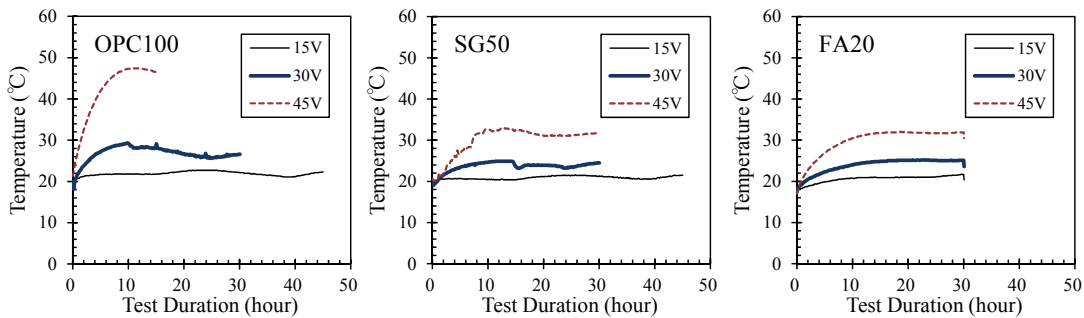**Figure 6. Electrical Current Passing through Specimens**



**Figure 7. Temperature in Catholyte Solution**

**Comparison of Chloride Migration and Diffusion Coefficients.** The chloride migration coefficient based on the PWRI recommendation, $D_{nssm,PWRI}$, and the chloride diffusion coefficient obtained from the immersion test, $D_{nss}$, are shown in **Figure 8**. $D_{nssm,PWRI}$ obtained in the specimens after the 91-day water curing procedure is presented in this figure. It is interesting to observe that both coefficients of the specimens with SCMs were lower than those of the specimens without SCMs although those two tests were based on completely different rationales and testing procedures. In other words, the use of SCMs proved to be effective for enhancing the resistance to chloride ingress using the two different tests.

Additionally, $D_{nss}$ is lower than $D_{nssm,PWRI}$ in all binder types. This gap between the two coefficients is likely to be induced by different curing conditions of the specimens used in those two tests before and/or during the test. While the non-steady-state migration test was performed on the specimens at the age of 91 days, the chloride profiles were measured in specimens immersed in NaCl solution for a 6-month period. Namely, the non-steady-state migration test evaluates the resistance of the specimens to chloride ingress immediately after the 91-day water curing procedure, and the immersion test investigates the resistance of specimens that were not only exposed but also cured in the NaCl solution for six months. The curing condition is known to provide substantial effects on the resistance to chloride ingress. Thus, it is reasonable to assume that the discrepancy between the two coefficients is attributable to differences in not only the rationales and testing procedures but also the curing conditions of the specimens before and/or during the test. Additionally, it should be noted that the effect of the difference in NaCl concentration of the salt solution used for the immersion test is negligible compared with the gap between those two coefficients.
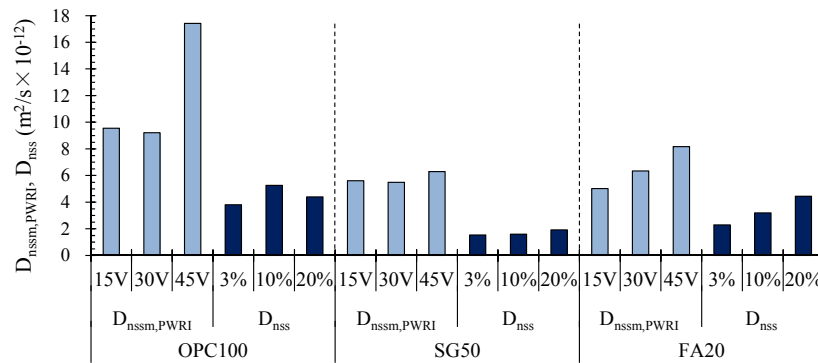
**Figure 8.  Comparison of Chloride Migration and Diffusion Coefficients**
Note: The chloride migration coefficients are presented for each binder type and applied voltage.
The chloride diffusion coefficients are shown for each concentration of NaCl solution.

## CONCLUSIONS

The non-steady-state migration test was performed on mortar specimens mixed with SCMs. The conclusions derived from this experimental program are summarized as follows.

(1) The use of more than one specimen with different test durations is recommended for obtaining reliable chloride migration coefficients in the non-steady-state migration test since the chloride migration rate decreased during the test. Additionally, the voltage applied to the specimens should be set at a value that prevents a substantial increase in electrical current and solution temperature during the test.

(2) Although the chloride migration coefficients derived from the non-steady-state migration test and the chloride diffusion coefficients obtained from the immersion test varied widely, both coefficients indicated that the mixing of SCMs contributed to the enhanced resistance of the mortar specimens to chloride ingress.

We are also conducting a long-term exposure test to investigate the applicability of different test methods to measure the resistance of SCM concrete to chloride ingress. Twenty-six types of concrete specimens with or without SCMs were fabricated at the Public Works Research Institute for this investigation. The test results derived from the long-term exposure test will be compared with those obtained from the non-steady-state migration test, immersion test, and steady-state migration test. This paper summarized preliminary test results that focused exclusively on the investigation of the non-steady-state migration test.

## ACKNOWLEDGEMENT

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