

## JSCE-G571-2003

### Test method for effective diffusion coefficient of chloride ion in concrete by migration

#### 1. Scope of Application

This standard specifies a migration test method for the calculation of the effective diffusion coefficient of chloride ion in concrete. A constant DC voltage is applied to the concrete, allowing chloride ion to migrate under steady state conditions. Note that this standard is not applicable to concrete containing steel fibers or any other conductive material.

#### 2. Referenced Standards

By being cited herein, the following standards constitute part of the definition of this standard. This standard is based on the latest version of these cited documents.

JIS A 1132	Method of making and curing concrete specimens
JIS A 1108	Method of test for compressive strength of concrete
JIS K 0101	Testing methods for industrial water
JIS A 5664	Tar epoxy adhesive
JIS K 8150	Sodium Chloride (Reagent)
JIS K 8576	Sodium Hydroxide (Reagent)

#### 3. Definitions

The following terminology is used in this standard:

- a) **Migration:** A phenomenon by which ions migrate into the pore solution of concrete under the influence of an electrical potential gradient.

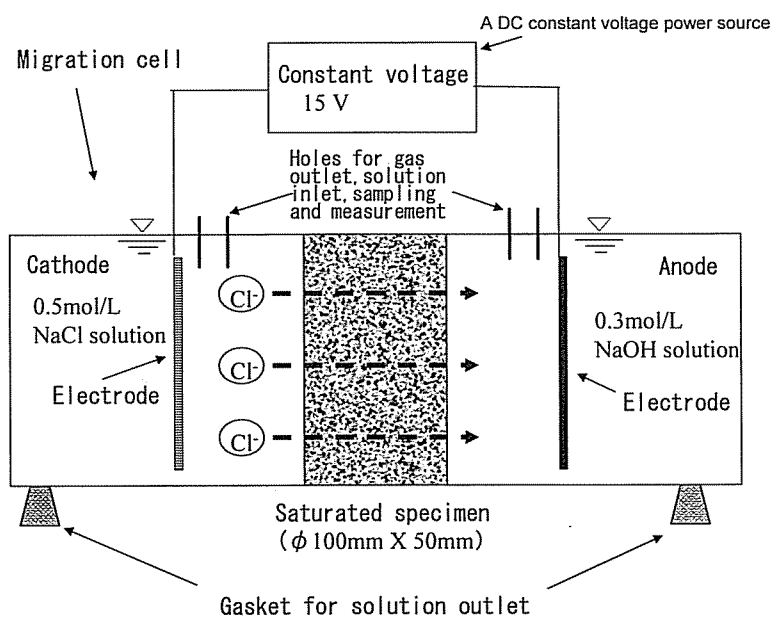


Fig.1 Migration cell equipment

- b) **Steady-state:** A condition in which the flux of passing ions is constant in time.
- c) **Migration-based effective diffusion coefficient:** A coefficient representing the degree of difficulty with which an ion migrates through the concrete pore solution. In this standard, chloride ions are the target ions. The migration-based effective diffusion coefficient for chloride ions is different from the apparent diffusion coefficient for all chloride ions, including immobilized ions. This coefficient is called the effective diffusion coefficient for short.

#### 4. Principle

As shown in **Fig. 1**, a concrete sample divides the anode and cathode of a migration cell. When a constant direct-current (DC) voltage is applied across the cell, negatively charged chloride ions migrate from the cathode toward the anode through the concrete pore solution. A steady state is assumed to be reached once the rate of chloride concentration increase in the anode section becomes constant, and the flux of chloride ions through the pore solution is then determined. This flux represents the degree of difficulty with which chloride ions pass through the pore structure. The effective diffusion coefficient of chloride ions can be calculated from the flux according to electrochemical principles, namely the Nernst-Planck Equation.

#### 5. Test Equipment

The equipment used for migration testing<sup>(1)</sup> is as follows:

**Note (1):** **Fig. 1** gives a typical schematic diagram of a migration test.

- a) The migration cell shall be manufactured of materials<sup>(2)</sup> resistant to the solution used in the test. A concrete specimen prepared according to the method given in Clause 6 (Test Specimens) of this standard shall separate the cathode and anode sections. The volume of the anode and cathode sections is approximately 1 liter. **Figures 2** and **3** give shape and size of a typical migration cell.

**Note (2):** Transparent acrylic material is recommended.

- b) The starting solution in the anode section shall be 0.5 mol/L of NaCl solution and in the cathode section 0.3 mol/L of NaOH solution, respectively<sup>(3)</sup>.

**Note (3):** The NaCl and NaOH shall be of quality similar to that specified in JIS K 8150 and JIS K 8576, respectively.

- c) The DC constant voltage power supply shall be capable of applying a constant DC voltage with a precision of  $\pm 0.1$  V<sup>(4)</sup>.

**Note (4):** The DC constant voltage power supply should have a 1 Amp rating.

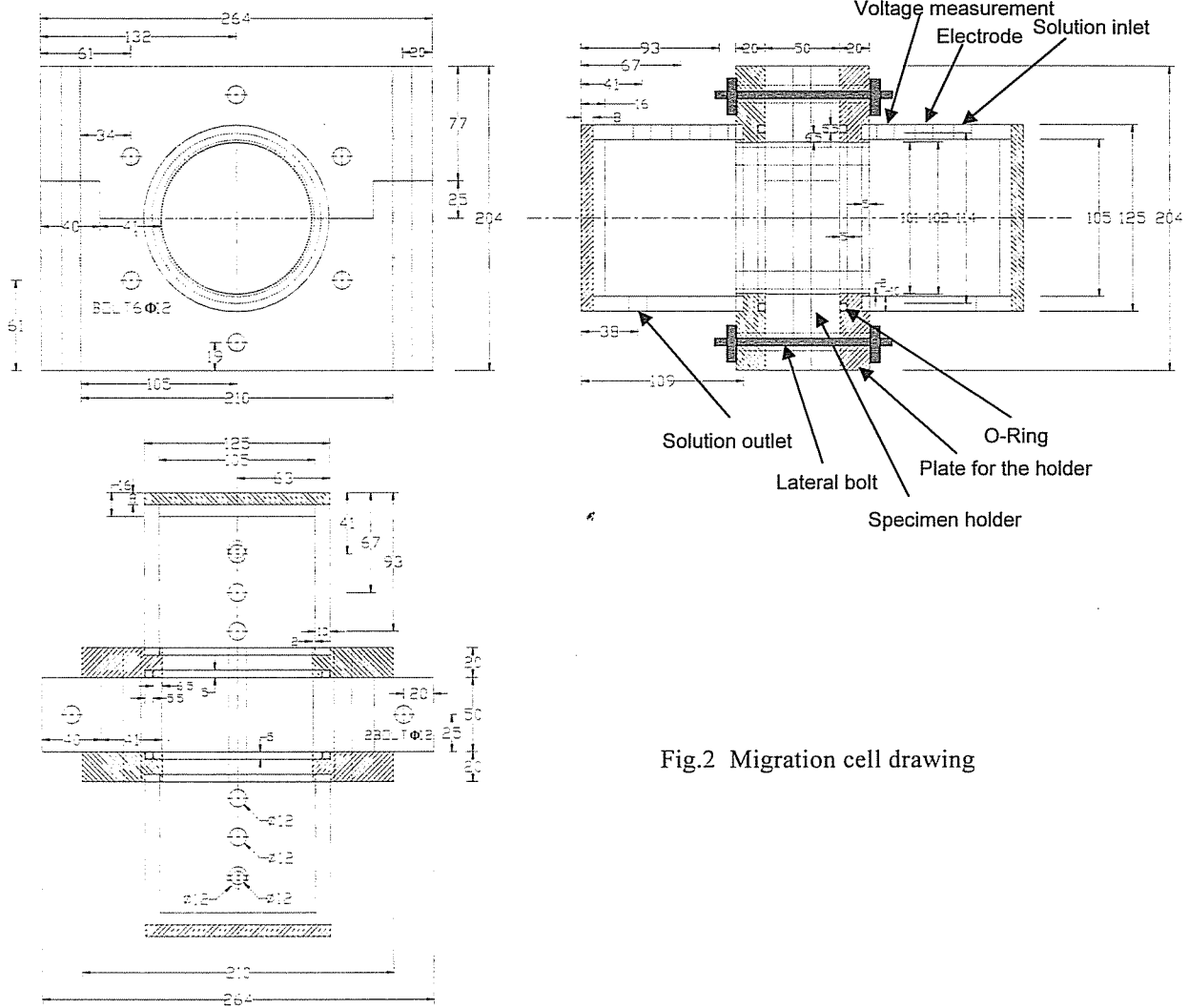


Fig.2 Migration cell drawing

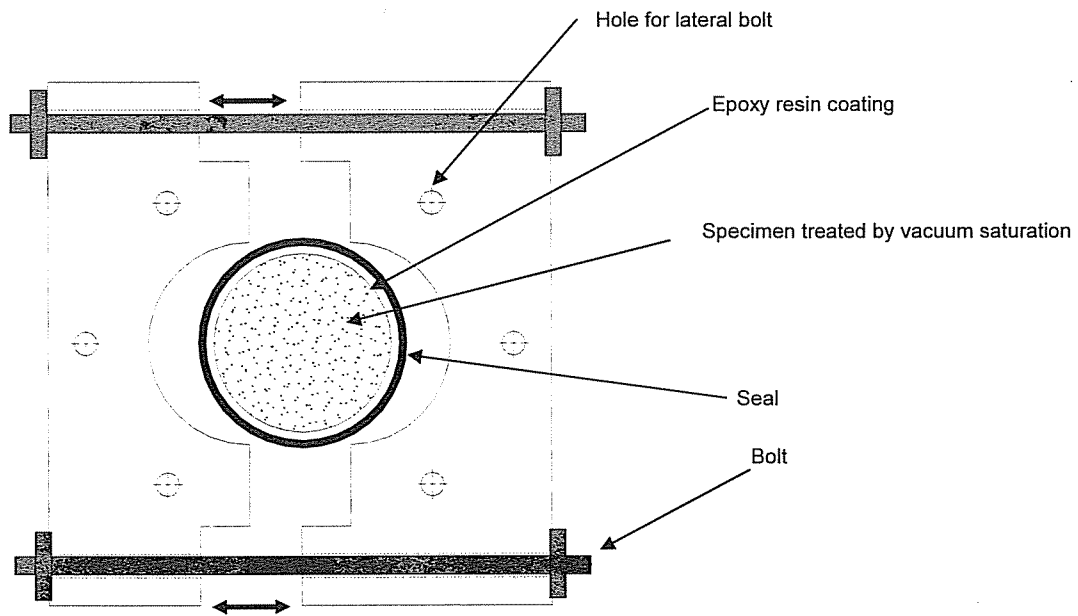


Fig.3 Specimen holder

- d) The anode and cathode electrodes in the migration cell shall remain electrochemically stable for the duration of the test. The electrode material must not affect the experimental results<sup>(5)</sup>. The electrodes shall be either circular or rectangular in shape, and their cross-sectional area shall be at least 60% of the cross-sectional area of concrete exposed to the cell solution.

**Note** <sup>(5)</sup>: Stainless steel may be used for the cathode, while a carbon plate, titanium plate, or platinum plate is suitable for the anode. Carbon is consumed with the passage of time and therefore shall be renewed after a number of tests.

- e) The thermocouple used to monitor temperature changes in the solution shall be watertight and resistant to the cell solution. It shall have a measurement range of approximately  $-10$  to  $+110^{\circ}\text{C}$  with a precision of  $\pm 1^{\circ}\text{C}$ .

- f) The potentiometer used to measure the actual potential gradient between the two concrete surfaces shall have a range of 0 to 99.9 V with precision of  $\pm 0.1\%$ .

## 6. Test Specimens

### 6.1 Specimen size

The test specimen shall be a concrete disk measuring 100 mm in diameter and 50 mm in thickness. The maximum size of coarse aggregate shall be 25 mm.

### 6.2 Specimen preparation

Test specimens shall be prepared as follows.

- a) Concrete cylinders measuring 100 mm in diameter and 200 mm in height shall be made according to JIS A 1132.
- b) After curing for the appropriate period<sup>(6)</sup> according to JIS A 1132, the cylinders made in a) above shall be sliced using a wet or dry diamond cutter into 50 mm slices. In doing this, end sections measuring 25 mm in thickness shall first be removed, then the remaining 150 mm section shall be cut to provide one or two disk specimens.

**Note** <sup>(6)</sup>: Standard curing is regulated as 28 days. However, this period may be adjusted as necessary according to the types of materials used and other factors.

- c) Specimen diameter and thickness shall be measured accurately according to JIS A 1108.
- d) Three disk specimens shall be prepared for each test.

### 6.3 Specimen pretreatment

The test specimens shall be pretreated according to the following procedure:

- a) Disk specimens prepared according to Clause 6.2 above shall be dried for about 4 hours at standard temperature and humidity ( $20\pm 2^{\circ}\text{C}$  and  $60\pm 5\%\text{RH}$ ) and then the circumference shall be coated with epoxy resin<sup>(7)</sup>.

**Note** <sup>(7)</sup>: Epoxy resin coating meeting the specifications of Type 1 in JIS K 5664 or equivalent shall be used. Although there is no specification of coating thickness, care shall be taken because an overly thick coating may lead to trouble with mounting the specimen in the migration cell.

- b) Once coated in epoxy resin, specimens shall be stored under standard conditions ( $20\pm 2^{\circ}\text{C}$  and  $60\pm 5\%\text{RH}$ ) for at least 4 days. For this duration, the exposed (uncoated) concrete surface shall be treated so as to prevent drying.

- c) In order to saturate the concrete with water, vacuum saturation shall be carried out according to the following procedure<sup>(8)</sup>.

- 1) The test specimen shall be placed vertically in a beaker within a vacuum desiccator.
- 2) The desiccator shall be evacuated with a vacuum pump for 3 hours with the inside pressure maintained at less than 150 Pa.
- 3) Before stopping the vacuum pump, distilled the beaker holding the test specimen shall be filled with distilled water until the specimen is submerged.
- 4) The vacuum pump shall be stopped once the beaker is filled with distilled water.
- 5) Air shall be admitted into the desiccator and left for a day or so.

**Note** <sup>(8)</sup>: If parts of the specimen remain unsaturated, errors will arise in the test results because ion permeability in unsaturated areas will be ignored.

#### 6.4 Mounting specimen in migration cell

The mass of the specimen shall be measured immediately after removal from the vacuum desiccator<sup>(9)</sup> and then the specimen shall be mounted in the migration cell. During this process, a seal shall be placed over the specimen contact surfaces to prevent leakage of cell solution.

**Note** <sup>(9)</sup>: The mass shall be measured to a precision of 0.1 g. When using a holder as shown in Fig. 3 to mount a test specimen in the migration cell, the combined mass of holder and specimen may be measured after mounting.

### 7. Test Procedure

#### 7.1 Migration test

The migration test shall be performed in accordance with the following procedure:

- a) The test shall be carried out a standard temperature of  $20\pm 2^{\circ}\text{C}$ .
- b) After mounting the test specimen in the migration cell, the cathode and anode sections shall be filled with their respective test solutions as described in Clause 5.b). In doing this, the volume of test solution shall be such that both surfaces of the test specimen are completely submerged. The solution

volumes ( $V^I$ : volume of cathode solution;  $V^{II}$ : volume of anode solution) shall be measured to a precision of 0.01 l. It shall be confirmed that there is no leakage of the solutions.

- c) A DC potential of 15 V shall be applied across the electrodes using a DC constant voltage power supply<sup>(10)</sup>.

**Note (10):** During the migration test, electrolysis of water will lead to small amounts of hydrogen and oxygen gas being produced at the anode and cathode, respectively.

- d) During the course of the migration test, the whole of the solution in the anode section shall be completely renewed appropriately so as to hold the chloride ion concentration in the anode section below 0.05 mol/l. Similarly, the whole of the solution in the cathode section shall be renewed appropriately so as to hold the chloride ion concentration in the anode section no lower than 0.45 mol/l.

**Remark:** In the anode section in particular it is important to control chloride ion concentration and pH in order to prevent the production of chlorine gas or hypochlorous acid gas. By completely replacing the solution periodically, the pH can be maintained at around 13.

- e) The migration test shall continue until the rate of chloride ion increase in the anode section becomes constant. In general, when five consecutive measurements of increase rate at a given interval give the same result, a steady state can be assumed and the test can be terminated.

## 7.2 Measurements and measurement methods

- a) During the migration test, electrical current<sup>(11)</sup>, electrical potential across the test specimen, solution temperature, and chloride concentration in the anode and cathode sections shall be measured at certain intervals<sup>(12)</sup>. Additionally, at termination of the test, the mass of the test specimen shall be measured<sup>(13)</sup>.

**Note (11):** Electrical current measurements are for monitoring purposes; if abnormal values are observed, it is necessary to check for leakage of solution between anode and cathode sides and for possible bad connections.

**Note (12):** The standard measurement interval is daily. However, if the concrete specimen has a low electrical conductivity, the interval may be increased.

**Note (13):** Mass shall be measured to a precision of 0.01 g. When using a holder as shown in **Fig. 3** to mount a test specimen in the migration cell, the combined mass of holder and specimen may be measured after mounting.

- b) In measuring the electrical potential across the test specimen, the + and – terminals of the potentiometer shall be inserted into the cathode and anode solutions, respectively, and the electrical

potential shall be measured as close as possible to the surface of the specimen without contact between specimen and terminals<sup>(14)</sup>. Terminals shall be inserted only at the time of measurement, and shall be removed from the solution at other times.

**Note** <sup>(14)</sup>: The electrical potential across the test specimen is less than the potential (15 V) applied to the electrodes; in general it is around 13 V.

- c) The temperature of the cell solution shall be measured using a thermocouple to confirm that it is equivalent to room temperature<sup>(15)</sup>.

**Note** <sup>(15)</sup>: If a higher temperature is observed, a possible cause is high electrical conductivity of the test specimen, leading to large current flow. The thermocouple shall be inserted into the solution only for the duration of measurements.

- d) Measurements of chloride ion concentration on the two sides of the migration cell shall be implemented by taking samples from the solution (5-10ml)<sup>(16)</sup>. In taking samples from the solution, it should be stirred well. As samples are withdrawn, it must be confirmed that both faces of the test specimen remain immersed. The chloride concentration in the sampling solution is measured according to JIS K 0101.

**Note** <sup>(16)</sup>: Although after sampling there is no need to replenish the amount taken as a sample ( $V_i$ ), this sampled value is used in calculating the flux as part of the calculation of test solution volume ( $V_t^I \text{ or } II = V^I \text{ or } II - \sum V_i$ ) in each cell ( $V_t^I \text{ or } II$ ). Although the volume of solution decreases slightly through electrolysis of the water, this loss can be ignored.

## 8. Calculation

### 8.1 Calculation of chloride ion flux

The flux of chloride ions in the steady state<sup>(17)</sup> is calculated using the following equation, and the value obtained is rounded to three significant digits.

$$J_{Cl} = \frac{V^{II}}{A} \frac{\Delta c_{Cl}^{II}}{\Delta t}$$

where,  $J_{Cl}$ : Flux of chloride ions in steady state (mol/(cm<sup>2</sup> year))

$V^{II}$ : Volume of anode solution (L)<sup>(18)</sup>

$A$ : Cross section of specimen (cm<sup>2</sup>)

$\Delta c_{Cl}^{II}/\Delta t$ : Rate of increase in chloride ion concentration on anode side ((mol/l)/year)<sup>(19)</sup>

**Note** <sup>(17)</sup>: The term “steady state” as used in this standard is the condition in which chloride ion concentration is increasing almost constantly, as indicated in Fig. 4.

**Note (18):** In calculating the flux of chloride ions in the steady state, the volume of solution on the anode side is taken to be the average solution volume during the period of the test.

**Note (19):** In determining the rate of increase of chloride ion concentration on the anode side, the accumulated concentration of chloride ion, in which newly measured concentration is added to the previously measured one before the replacement of solution, is used. Figure 4 shows an example of the change in chloride ion concentration with time by this method.

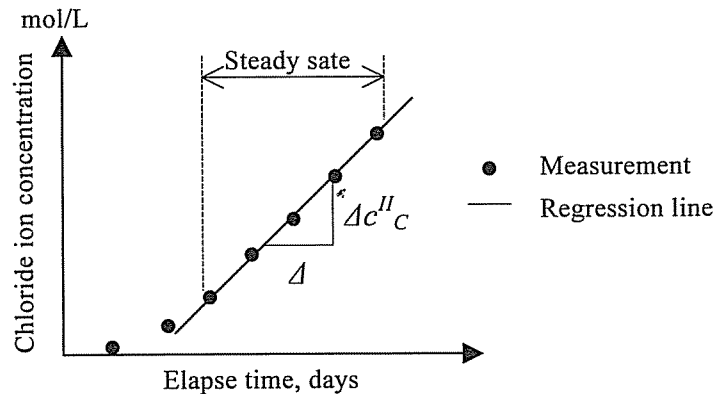


Fig. 4 Change in chloride ion concentration on the anode side with time

## 8.2 Calculation of effective diffusion coefficient of chloride ion

The effective diffusion coefficient of chloride ion in the concrete is calculated using following equation, and the result is rounded to three significant digits:

$$D_e = \frac{J_{Cl}RTL}{|Z_{Cl}|FC_{Cl}(\Delta E - \Delta E_c)} \times 100$$

where,  $D_e$ : Effective diffusion coefficient ( $\text{cm}^2/\text{year}$ )

$R$ : Gas constant ( $= 8.31 \text{ J}/(\text{mol} \cdot \text{K})$ )

$T$ : Absolute temperature (K) (19)

$Z_{Cl}$ : Charge of chloride ion ( $= -1$ )

$F$ : Faraday constant ( $= 96,500 \text{ C}/\text{mol}$ )

$C_{Cl}$ : Measured chloride ion concentration on cathode side (mol/l)

$\Delta E - \Delta E_c$ : Electrical potential difference between specimen surfaces (V)(20)

$L$ : Length of specimen (mm)

**Note (20):** Absolute temperature, chloride ion concentration on the cathode side, and potential difference between specimen surfaces, as necessary in calculating the effective diffusion coefficient, are values obtained by averaging measurements made in the steady state.



## 9. Report

### 9.1 Compulsory reporting

The report must give the following information:

- a) Materials and mix proportion of specimen
- b) Size of specimen
- c) Curing condition and period; days cured before testing
- d) Change in solution volume on anode side with time (remaining volume after each sample) and the average value in the steady state
- e) Change in chloride ion concentration on the anode side with time (Fig. 4) and rate of chloride ion concentration increase in the steady state
- f) Calculated flux in the steady state
- g) Changes in electrical current and solution temperature with time
- h) Change in chloride ion concentration on anode side solution with time and average value in the steady state
- i) Change in electrical potential difference between specimen surfaces and average value in the steady state
- j) Effective diffusion coefficient calculated by the method described for the migration test<sup>(21)</sup>

**Note <sup>(21)</sup>:** This value is obtained from tests on three disk specimens, yielding three sets of calculation results that are averaged to obtain the final value. If the required results cannot be obtained with any specimen, the test must be repeated. The electrical current or change in electrical current in the initial stage can be shown as a correction to the test. In this case, a different specimen must be used for the new test.

- k) Measurement date, month, and year
- l) Institution carrying out measurement

### 9.2 As-needed reporting

The report should give the following information where relevant:

- m) Change in solution volume on cathode side with time (remaining volume after each sample)
- n) Times of solution renewed
- o) Weight change of specimen before and after test
- p) Apparent diffusion coefficient of chloride ion in concrete calculated from the effective diffusion coefficient obtained through the migration test<sup>(22)</sup>

**Note <sup>(22)</sup>:** This value is calculated according to “Appendix: Calculation of apparent diffusion coefficient from effective diffusion coefficient obtained through the electric migration test”.

## Appendix : Calculation of apparent diffusion coefficient from effective diffusion coefficient obtained through the migration test

### 1. Scope

This appendix provides a method of calculating the apparent diffusion coefficient of chloride ion in concrete from the effective diffusion coefficient obtained in a migration test.

**Remark:** Migration tests are normally carried out on concrete with considerable resistance to chloride ion penetration, and directly determining the apparent diffusion coefficient would require an unacceptably long submersion in salt water. However, the effective diffusion coefficient obtained through a migration test is different from the apparent diffusion coefficient. Therefore, a method of converting an effective diffusion coefficient into an apparent diffusion coefficient is necessary.

### 2. Definitions

The following terminology is used in this appendix:

- a) **Apparent diffusion coefficient of chloride ion:** A coefficient that defines the diffusion rate of all chloride ions in the concrete when driven by a concentration gradient in the concrete pore solution while some remain fixed to the hardened cement. Known in this appendix as the “apparent diffusion coefficient”.
- b) **Total chloride ions:** The quantity of chloride ions extracted from concrete by nitric acid, including all chloride ions present in the pore solution of the hardened concrete, sodium chloride, and fixed chlorides.

### 3. Calculation method

The method of calculation is as follows:

#### 3.1 Conversion to apparent diffusion coefficient from effective diffusion coefficient

The apparent diffusion coefficient is calculated using the following equation, and the value obtained is rounded to three significant digits:

$$D_{ae} = k_1 \cdot k_2 \cdot D_e$$

where,

- $D_{ae}$ : Apparent diffusion coefficient as calculated from the effective diffusion coefficient obtained in a migration test (cm<sup>2</sup>/year)
- $D_e$ : Effective diffusion coefficient obtained in migration test (cm<sup>2</sup>/year)
- $k_1$ : Coefficient reflecting the equilibrium concentration of chloride ion on the cathode side and that at the concrete surface<sup>(1)</sup>
- $k_2$ : Coefficient reflecting the effect of immobilization of chloride ions in the hydrated cement system.

**Remark:** The apparent diffusion coefficient as converted from the effective diffusion coefficient obtained in a migration test is not always equal to the value determined according to JSCE-G572-2003 “Test method for apparent diffusion coefficient of chloride ion in concrete by submergence in salt water” or by JSCE-G573-2003 “Measurement method for distribution of total chloride ions in a concrete structure”. For this reason, the apparent diffusion coefficient calculated in this appendix is differentiated from these values and expressed as  $D_{ae}$ : apparent diffusion coefficient converted from effective diffusion coefficient obtained in a migration test.

**Note<sup>(1)</sup>** This coefficient is necessary so as to convert the concentration of mobile chloride ions present in the pore solution near the contact NaCl solution into a quantity of chloride ions per unit volume of concrete.

### 3.2 Derivation of $k_1, k_2$

Coefficients  $k_1$  and  $k_2$  vary with the type of cement and the quantity of cement hydration products in the concrete. In general, these coefficients tend to be smaller as the concentration of chloride ions freely migrating in the pore solution of the concrete is reduced, partly as a result of chloride ion immobilization. Where the quantity of immobilized chloride ions and the concentration of freely migrating chloride ions have a linear relation, then  $k_1 \cdot k_2$  may be calculated using the following equation:

$$k_1 \cdot k_2 = \frac{1}{\varepsilon} \cdot \left( 1 - \frac{C_b}{C_{total}} \right)$$

where,  $\varepsilon$ : Porosity of concrete ( $\varepsilon = V_{pore}/V_c$ )

$V_{pore}$ : Volume of pores in concrete<sup>(2)</sup>

$V_c$ : Volume of concrete

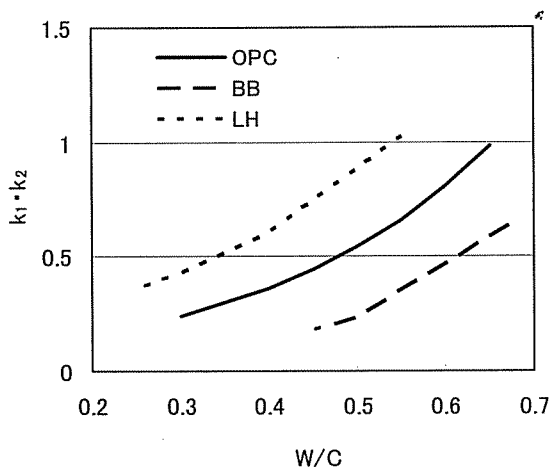
$C_b$ : Quantity of immobilized chloride ions in concrete

$C_{total}$ : Total quantity of chloride ions in concrete

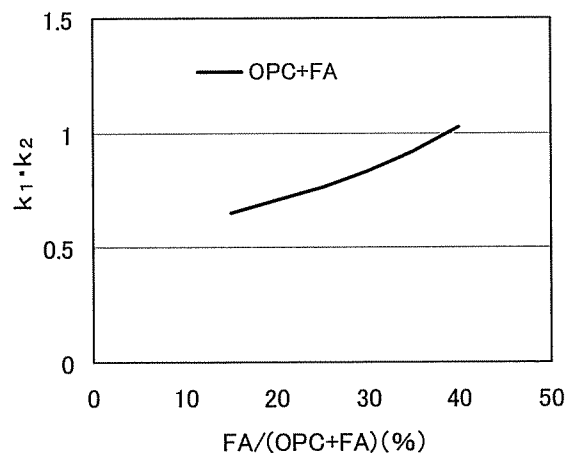
**Remark:** If the concentration of chloride ion in the concrete pore solution is assumed to be equal to that on the cathode side, then  $k_1$  may be theoretically given as the reciprocal of the concrete porosity. However it is difficult to specify which pores can be freely passed by chloride ions, so the porosity used in the calculation may not be suitable for the determination of  $k_1$ . This shall be taken into account in determining  $k_1$ . In contrast,  $k_2$  may be considered identical to  $(1 - C_b/C_{total})$  if the quantity of immobilized chloride ions has a linear relation with the concentration of diffusing chloride ion in the concrete. In the other words,  $k_2$  may be determined from the ratio of immobilized chloride ions to total chloride ions ( $C_b/C_{total}$ ) in the concrete. However, has been noted that the range of validity of this linear relation is limited. Therefore,  $k_2$  also shall be determined specifically.

Reference Fig.1 and Reference Fig.2 may be used for the determination of  $k_1 \cdot k_2$  depending on the type of cement, the water-to-cement ratio, and the ratio of cement replacement by mineral additives. These relationships are based on empirical formulas and have been experimentally obtained by comparing effective diffusion coefficients obtained in migration tests with apparent diffusion coefficients. The apparent diffusion coefficients were determined for similar concrete mixes by submergence tests in salt water with immersion times of 1 year or longer.

**Note<sup>(2)</sup>** :Technically speaking, this means the volume of pores in which chloride ions are able to migrate.



Reference Fig.1 Determination of  $k_1 \cdot k_2$  with W/C for a binder type of OPC, BB, or LH



Reference Fig.2 Determination of  $k_1 \cdot k_2$  with the ratio of FA/(OPC+FA)