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## **CONCRETE, MORTAR AND CEMENT BASED REPAIR MATERIALS: CHLORIDE DIFFUSION COEFFICIENT FROM MIGRATION CELL EXPERIMENTS**

Key words: concrete, mortar, repair materials, diffusion coefficient, chloride migration, test method

### **SUMMARY**

The steady state chloride ion diffusion coefficient of concrete, mortar and cement based repair materials is determined by an accelerated laboratory test method. The amount of chloride vs. time passing through a porous material exposed to a constant direct voltage is measured after steady state is reached, in order to calculate a chloride diffusion coefficient.

### **1 SCOPE**

This method specifies an accelerated laboratory method to determine the steady state chloride ion diffusion coefficient of porous, cement-based materials.

### **2 FIELD OF APPLICATION**

The method can be used to determine the steady state chloride diffusion coefficient for concretes, mortars and cement based repair materials as a measure of their relative diffusivity after chloride binding is saturated. This diffusion coefficient can not be compared directly with non-steady state diffusion coefficients or used in service life predictions where chlorides diffuse in a non-steady manner or are transported by absorption [3].

### **3 REFERENCES**

- [1] NT BUILD 355, approved 1989-11.
- [2] Andrade, C.: "Calculation of Chloride Diffusion Coefficients in Concrete from Ionic Migration Measurements". Cement and Concrete Research, Vol. 23, No. 3, 1993, pp. 724-742.
- [3] Rodum, E. and Justnes, H.: "Chloride Ion Diffusion Coefficients for Concrete - A Review of Experimental Methods", Proc. 10th Int. Cong. on the Chemistry of Cement, Gothenburg, Sweden, 2-6 June 1997, 10 pp.

### **4 DEFINITIONS**

Chloride migration is the movement of chloride ions through a porous specimen due to an imposed electrical field. Chloride diffusion is the movement of chloride ions through a porous specimen due to concentration differences.

### **5 SAMPLING**

The test is carried out on specimens of 95-100 mm diameter and 50 mm thickness, sliced from cylinders.

The test may be carried out on both cast and drilled cylinders of minimum length 200 mm.

Cast cylinders should be demoulded 1 day after casting, and cured in water ( $20\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ ) until 90 days of age.

Repair materials should be mixed and cured according to specifications from the manufacturer.

### **6 TEST METHOD**

#### **6.1 Principle**

This method determines the amount of chloride passing through a specimen by applying a constant direct (DC) voltage of minimum 12 volt across the specimen, but not so high that the temperature generated in the specimen exceeds  $40\text{ }^{\circ}\text{C}$ . The chloride ions migrate from the NaCl solution compartment at the negative side of the specimen to the NaOH solution compartment at the positive side. The chloride flux through the specimen is determined as the increase in chloride concentration with time in the NaOH solution compartment after steady state is achieved, and the chloride diffusion coefficient is calculated.



## 6.2 Apparatus and equipment

- Migration cell (as in Fig. 3, Chapter 7, or equivalent design)
- Epoxy coating materials or equivalent
- Water-cooled diamond saw
- DC voltage power source
- DC amperemeter
- Reference electrodes
- Thermocouple
- Chloride analysing equipment
- Chemicals ( $\text{Ca}(\text{OH})_2$ , NaOH, NaCl, distilled or deionised water)
- Balance
- Resistance measurement equipment (optional).

## 6.3 Preparation of test specimen

The cylinder is immersed in saturated  $\text{Ca}(\text{OH})_2$ -solution at  $20 \pm 2$  °C in a tightly closed tank. The tank must be filled to the top to minimise carbonation of the liquid. The next day the mass is determined by weighing the cylinder in surface-dry condition. Surface-dry condition is obtained by wiping the cylinder with a wrung cloth wetted with the liquid in which the cylinder has been immersed. The storage in the saturated  $\text{Ca}(\text{OH})_2$ -solution continues until the mass does not change more than 0.1 % per day. The cylinder is then dried in air ( $50 \pm 5$  % RH and  $20 \pm 2$  °C) for 4 hours before the side surface of the cylinder is cast in epoxy, in such a way that the total diameter can fit into the migration cell, e.g. 109 mm (see Fig. 1). The epoxy is allowed to cure. Impermeable coatings other than epoxy might be used as well.

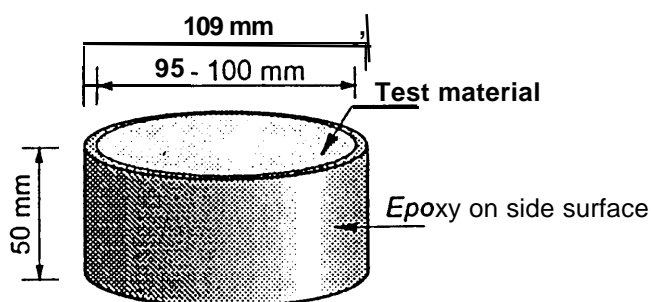


Figure 1. Test specimen.

When the epoxy is hardened the cylinder is sliced into a minimum of 3 parallel specimens. Slice thickness, 50 mm (obtained thickness =  $l$  in Eq. (2)), and diameter (to calculate  $A$  in Eq. (1)) are measured accurately. One specimen is prepared from the top with the cut surface 10 mm from the cast surface, one from the middle and one from the bottom of the sample. Each specimen should be marked clearly to identify the relative position within the sample.

After cutting, the specimens are immersed in the  $\text{Ca}(\text{OH})_2$ -solution until the mass stabilises as described above.

## 6.4 Procedure

The specimens are kept in the  $\text{Ca}(\text{OH})_2$ -solution until testing. Prior to mounting the specimen, it is recommended that the electrical resistance should be measured using AC at frequency  $> 100$  Hz. The measurement should be repeated after the chloride migration test, and compared with the initial value as a control of changes in pore water chemistry. Furthermore, the specimen (including epoxy) should be weighed before and after the experiment as a control of additional pore filling and/or salt enrichment due to osmosis.

Steel mesh is placed in each half-cell compartment and the specimen is mounted according to Fig. 3a. An appropriate sealant material may, if necessary, be applied on the specimen circumference.

Fill both compartments with saturated  $\text{Ca}(\text{OH})_2$ -solution and leave the cell undisturbed for 20-24 hours. Check for leakage. Empty both compartments and seal any leakage with appropriate sealant material. At this point the volume of compartment 2,  $V_2$  should be determined experimentally by for instance weighing the cell before and after filling.

Fill the negative (-) side of the cell with  $C_1 = 31.4$  kg  $\text{Cl}^-/\text{m}^3$  (i.e. 5 % NaCl solution or 51.7 g NaCl/l solution). Fill the positive (+) side of the cell with 0.3 N NaOH solution (1.2 % or 12 g NaOH/l solution).

Plug both holes on each of the compartments to prevent evaporation during the test period. If necessary, compartment 1 should be replenished with NaCl solution to maintain  $C_1$  approximately constant (within 95 % of initial value) during the entire experiment.

Connect wires to the stainless steel meshes, ammeter and power supply. Turn on the power supply and set to the fixed voltage,  $U$  (e.g. 12 V DC)  $\pm 0.1$  V. If a significantly higher voltage than 12 V is used, the temperature may differ from ambient due to heat generation.  $T$  must then be measured with a thermocouple next to the specimen surface and the recorded value used in Eq. (2). The temperature must not exceed 40 °C.

The voltage drop across the specimen,  $E$ , is measured by using two reference electrodes (e.g. Ag/AgCl with KCl) which are inserted into each compartment through the sampling hole, or by lugging capillaries close to the specimen surface.

For further information it is recommended to measure the current and also the resistance across the specimen during the experiment.

A qualitative chloride test is used until chloride penetration, consisting of periodically adding a drop of the liquid from the NaOH compartment to a test tube with slightly acidified (i.e.  $\text{HNO}_3$ ) 1 M  $\text{AgNO}_3$ . When a white precipitate can be observed, then determine the chloride content of the NaOH solution compartment at least once a day over a minimum of 7 days by a standardised method. The volume of liquid taken from the compartment should be replaced by NaOH solution between each sampling and the subsequent decrease in chloride concentration corrected by calculation. Linear regression analysis should utilise a minimum of 5 points of the linear part of the curve, and the linear correlation coefficient  $r^2$  should be at least 0.9.

Before ending the test, measure the voltage drop across the specimen, E.

After the end of the test, remove the specimen and rinse the cell. Weigh the specimen and measure the electrical resistance if this recommended procedure was followed from the start.

### 6.5 Expression of results

The chloride flux, J (steady state), through the specimen measured by the slope of the linear increase in chloride concentration in compartment 2 (NaOH-solution), C<sub>2</sub>, with increasing time, t (shown in Fig. 2):

$$J = \frac{C_2 V_2}{tA} \tag{1}$$

The diffusion coefficient is expressed according to Eq. (2) (from [2] but excluding the proposed activity coefficient for chloride ions):

$$D = \frac{JRT}{z_{Cl} F E C_1} \tag{2}$$

The values of chloride coefficients obtained by the former standard [1], D<sub>old</sub>, can be transformed into coefficients according to the present revision by:

$$D = \frac{RTD_{old}}{z_{Cl} F \Delta E} \tag{3}$$

where for Eqs (1), (2) and (3):

- D = diffusion coefficient [m<sup>2</sup>/s]
- E = voltage drop across specimen (average of values before and after test period) [V]
- l = concrete disc thickness [m]
- A = Concrete disc area [m<sup>2</sup>]
- C<sub>1</sub> = chloride concentration in compartment 1 [kg/m<sup>3</sup>] or [mole/l]
- V<sub>2</sub> = volume of compartment 2 [m<sup>3</sup>]
- z<sub>Cl</sub> = absolute value of electrical charge of chloride species (z<sub>Cl</sub> = 1) [equivalent/mole]
- F = Faraday number = 96,500 [C/equivalent]
- R = gas constant = 8.314 [J/mole·K]
- T = absolute temperature [K]

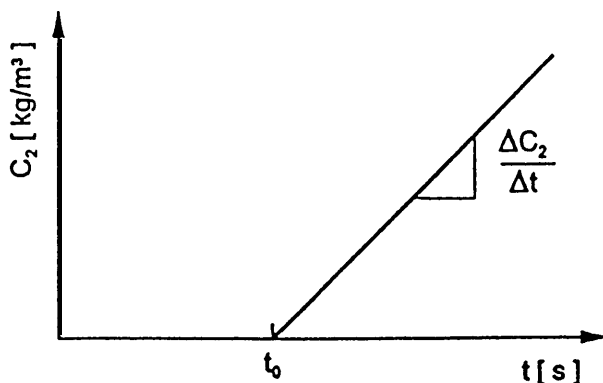


Figure 2. Schematic variation of chloride concentration with time in compartment 2.

### 6.6 Accuracy

The method yields a diffusion coefficient which is known [3] to be rather close (or at least the same order of magnitude) to the coefficient from pure steady state diffusion experiments when C<sub>1</sub> = 31.4 kg Cl<sup>-</sup>/m<sup>3</sup> (i.e. 5 % NaCl) and U > 10 V.

It is recommended to document the correlation further if more acceleration by additional increase in C<sub>1</sub> and/or U is applied.

### 6.7 Test report

The test report shall include the following information, if relevant:

- a) Name and address of the testing laboratory
- b) Identification number of the test report
- c) Name and address of the organisation and/or the person who ordered the test
- d) Purpose of the test
- e) Method of sampling and other circumstances (date and person responsible for the sampling)
- f) Name and address of manufacturer or supplier of the tested object
- g) Name or other identification marks of the tested object
- h) Description of the tested object
- i) Date of supply of the tested object
- j) Date of the test
- k) Test method
- l) Conditioning of the test specimen's environmental data during the test (temperature, time, RH etc)
- m) Identification of the test equipment and instruments used
- n) Any deviations from the test method
- o) Test results (use SI units); J, V<sub>2</sub>, A, C<sub>1</sub>, U, E, l, T, r<sup>2</sup> and D
- p) Optional information; electrical resistance, mass of each specimen before and after test, inaccuracy, uncertainty of the test results, etc.
- q) Date and signature.



APPENDIX

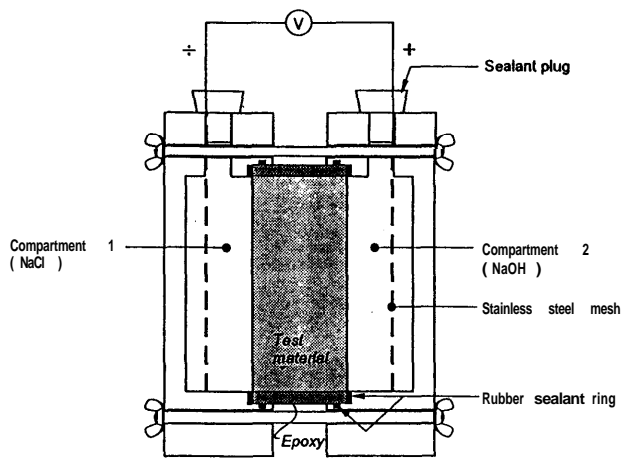


Figure 3a. Schematic view of test cell and mounted specimen.

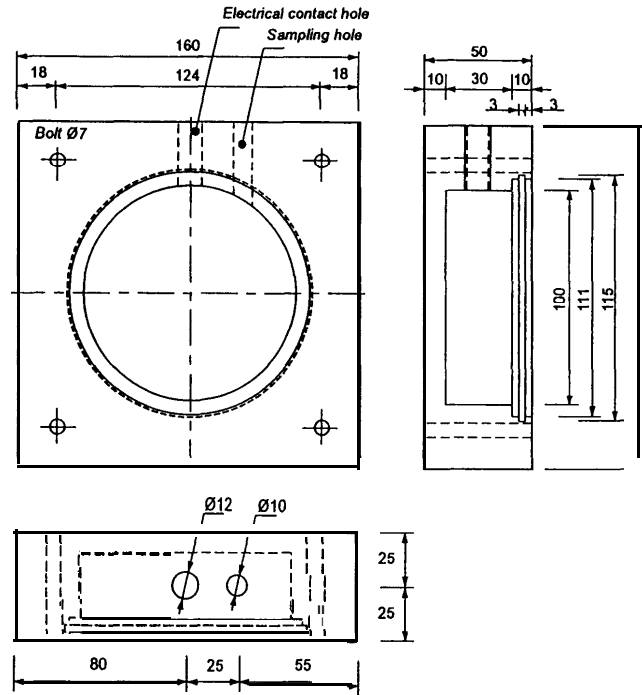


Figure 3b. Construction drawing of one half of the test cell.