APPENDIX A:
EXPERIMENTAL PROCEDURE FOR ESTIMATION OF CHLORIDE PENETRATION PARAMETERS

A.1 Estimation of chloride binding parameters: K_{eq} and $[Cl^-(s)]_{sat}$

The rate of chloride binding in concrete can be described by the following equation:

$$r = k_a [Cl^-(aq)] ([Cl^-(s)]_{sat} - [Cl^-(s)]) - k_a [Cl^-(s)] / K_{eq} \quad (A.1)$$

At steady-state (equilibrium) the rate vanishes, resulting in the following (inversely linear) relation between the steady-state concentrations:

$$\frac{1}{[Cl^-(s)]_\infty} = \frac{1}{[Cl^-(s)]_{sat}} + \frac{1}{K_{eq}[Cl^-(s)]_{sat}} \frac{1}{[Cl^-(aq)]_\infty} \quad (A.2)$$

Eq. (A.2) allows experimental determination of the parameters K_{eq} and $[Cl^-(s)]_{sat}$, through linear regression on measurements of pairs of values of steady-state concentrations $[Cl^-(aq)]_\infty$ and $[Cl^-(s)]_\infty$ taken on the same material for different initial chloride concentrations, as follows:

1. Sample Preparation: The specimens can be pastes (recommended), mortar, or concrete, cured at least for 3 months in saturated lime water (20^{o}C). After the curing period, they placed into an oven at 105 ^{o}C until complete drying (checking by weight stabilization). A representative part from each different specimen is coarsely crushed and all the material is ground to provide samples with particle size less than 2 mm (but not much lower than 0.2 mm). During the preparation, carbonation and overheating should be avoided. The powders are homogenized and can be kept in an oven at 105 ^{o}C until testing.

2. Test Procedure: Sodium chloride (NaCl) solutions with chloride concentrations of 0.05, 0.2, 1, and 5 mole/litre are prepared (e.g., 1.46, 5.84, 29.22, and 146.11 g NaCl, respectively placed in 500-ml glass volumetric flasks and filled by water up to the indication). A representative quantity of 10 g of the sample is put in a glass container and filled with 15 ml of NaCl solution. Thus, at least 4 combinations are prepared for each sample. However, additional chloride concentrations may be used extending the experimental accuracy. The containers are sealed and stored at 20 ^{o}C for two weeks to reach binding equilibrium. From time to time, and especially during the first 24h, the containers should be well-shaken ensuring satisfactory mixing.

3. Chloride Analysis: A quantity of 2-5 g solution is received from the containers by filtration. The chloride concentration in the solution can be determined by the Volhard titration method in accordance with the Nordic standard NT Build 208 (1984), and it is expressed as % Cl^- by weight of solution.

4. Calculations: The steady-state concentrations $[Cl^-(aq)]_\infty$ and $[Cl^-(s)]_\infty$ are calculated as:

$$[Cl^-(aq)]_\infty = \frac{\chi}{100}\rho_{sol} \qquad \text{:free chlorides} \qquad (A.3)$$

$$[Cl^-(s)]_\infty = \left([Cl^-(aq)]_0 - \frac{\chi}{100-\chi}\delta_{sol}\right)\frac{V_{sol}\rho_s}{m_s} \qquad \text{:bound chlorides} \qquad (A.4)$$

where, χ: % Cl^- by weight of solution (i.e., χ kg Cl^- /100 kg solution; measured), ρ_{sol}: density of the solution (kg/m^3 solution; given in reference 38), $[Cl^-(aq)]_0$: initial chloride concentration in the solution (kg/m^3 solution; given in Table A.1), δ_{sol}: initial water content of the solution (kg H_2O/m^3 solution; given in Table A.1), V_{sol}: volume of the solution (15.10^{-6} m^3), m_s: sample mass (10.10^{-3} kg), and ρ_s: density of the initial paste or mortar specimen at a dry condition (it has to be determined; about 2200 kg/m^3).

5. Parameter Estimation: Through linear regression of $1/[Cl^-(s)]_\infty$ (y) versus $1/[Cl^-(aq)]_\infty$ (x) results, the parameters are estimated from the slope and intercept as follows:

$$y = a\,x + b, \qquad [Cl^-(s)]_{sat} = 1/b, \qquad K_{eq} = b/a \qquad (A.5)$$

Table A.1 Parameter values for calculations*.

Chloride Solution, (mole/litre)	$[Cl^-(aq)]_0$ ($kgCl^-/m^3$ solution)	δ_{sol} (kg H_2O/m^3 solution)
0.05	1.775	997.4
0.2	7.1	994.8
1	35.5	980.1
5	177.5	893.6

*These values, as well any others for different initial chloride concentrations can be found in Reference 38.

A.2 Determination of intrinsic chloride diffusivity, D_{e,Cl^-}

1. Test Procedure: Long-term ponding experiments have to be performed, according to nordtest method NT Build 443 (1995). Prior to the immersion in the chloride solution, the samples (concrete or mortar cylinders or prisms) are coated by epoxy resin and then a slice of 10 mm thick from one end is removed. The samples are immersed in a chloride solution (165g NaCl/l solution) for at least 100 days (t_{max}). The temperature is kept constant at 20°C throughout the entire test period. At the end of the immersion period, the exposed surface is ground using a dry process in a diameter of 75 mm receiving thin successive layers from different depths (i.e., 1-2, 3-4, 5-6, 8-10, 12-15, 18-21, and 21-24 mm from the external surface) and yielding the chloride profile at that particular time. The total chloride content of the powders is determined by the Volhard titration method in accordance with the Nordic standard NT Build 208 (1984), and it is expressed as % Cl^- by weight of dry concrete (or mortar).

2. Calculations: The total chloride concentration $[Cl^-(t)]$ is calculated as follows (in kg/m^3 concrete):

$$[Cl^-(t)] = \frac{\chi \rho_S}{100 - \chi} \qquad \text{:total chlorides} \qquad (A.6)$$

where, χ: % Cl^- by weight of dry concrete (i.e., χ kg Cl^- /100 kg dry concrete; measured), and ρ_s: density of the initial concrete or mortar specimen at a dry condition (it has to be determined; about 2200 kg/m^3).

3. Diffusivity Estimation: Solving Eq. (6.2.1)-(6.2.4) for the parameter values of this case, i.e.,

K_{eq} and $[Cl^-(s)]_{sat}$: determined as previously or calculated by Eq. (6.2.8) and (6.2.9),
ε: measured or calculated by Eq. (3.2.17), (3.2.28), (3.2.35) or (3.2.43)
$[Cl^-(aq)]_0$= 100 kg/m^3,
M: specimen length, t_{max}=100 days,
time-step: 60-600 sec, cells in space N: 100 (i.e., space-step: M/N),

and using an initial value for D_{e,Cl^-} estimated approximately by Eq. (6.2.5) and (6.2.6), the total concentration of chlorides (i.e., $[Cl^-(t)]=\varepsilon[Cl^-(aq)]+[Cl^-(s)]$) is calculated. For the solution of these equations, the program EUCON should be used (see *user's manual*). The calculated profile is compared with the experimental values, and a new diffusivity value is taken to improve fitting. This procedure is repeated until satisfactory fitting of the model predictions to the experimental results, yielding an *optimum value* for the intrinsic diffusivity parameter (a least-square optimization technique may be used).