Abstract
A new method for operating chlorides electrodiffusion test is proposed. This method allows getting chlorides flux through the sample in steady state by using current transfer, which are obtained from a chronoamperometry. A comparison of results obtained by the model with those obtained by a classical dosage of chlorides in the downstream solution of the cell has been carried out for mortars and cement pastes. The model results seem to be closer to those of experimental dosage. We showed that it is not necessary to measure chloride concentration in upstream or downstream cell, but a simple chronoamperometry suffices to obtain transfer characteristics of the material tested.

1. Introduction
The corrosion of the reinforcement bars by chlorides diffusion is the most significant cause, which reduces the service life of reinforced concrete structures [1-2]. To predict or to improve this service life, it is necessary to master the transfer mechanisms of chlorides in concrete.

As the diffusion process is slow, electrical field is often applied to the sample to accelerate the phenomenon and to rapidly obtain the diffusion coefficient value. This diffusion coefficient is usually obtained from models based on the modified Fick’s second law [3-4]. By its global approach, this law assumes a transfer in a homogeneous medium that does not take into account electrochemical phenomena happening at the interface between the pore wall and the pore solution, arising from the electrical double layer. Studies [5-8] have indicated the influence of this double layer on the electrodiffusion process. The electrical double layer effect is qualitatively noted in these works, but it is not taken into account quantitatively neither in transfer modelling, nor in analysis of experimental tests.

The aim of this article is then to propose a model that integrates the electrical double layer in calculating current transfer due to chloride migration. Then, a chronoamperometry suffices to calculate chloride flux through a concrete or mortar sample.
2. Theoretical considerations

2.1 Modelling of electrical double layer

The interface between the solid phase and the pore solution can be modelled by the electrochemical decomposition shown in figure 1. That extends the Stern’s model for semi-conductors to mortars and concretes.

According to Antropov [9], the interface comprises several layers. At the electrolyte side, the plane passing by the centre of the first ions layer in contact with the solid interface (Σ) is called ‘the closest approach plane’. Its distance \(d_0\) is around 0.5 nm. The zone included between the solid interface and the closest approach plane is called the Helmholtz’s layer. In the zone going from the closest approach plane to the electrolyte centre (diffuse layer), Gouy assimilates ions to points charges forming a real space charge. In the solid phase, electrons are distributed also following the Gouy’s distribution. The three layers can be assimilated to condensers with respective capacities \(C_{H}, C_{G}, C_{S}\), associated in series, with equivalent capacity:

\[
\frac{1}{C_{SH}} = \frac{1}{C_S} + \frac{1}{C_H} + \frac{1}{C_G}
\]

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electron which goes into the solid phase. This phase is then charged at the surface and chloride atoms are adsorbed by the solid phase. The density of this charge is composed of surface charge densities: \( q \), engendered by the basic electrolyte and \( q_s \) by the addition of NaCl. The material (mortar or concrete) being a poor conductor, \( q \) and \( q_s \) cannot be constant; they are functions of time and space variables [10].

### 2.2 Local and macroscopic transfer equations

The modelling is carried out with electrical magnitudes in the aim of extracting the transfer current due solely to chloride electrodiffusion. Figure 2 shows the principle of chloride electrodiffusion test in cementitious materials. During this test, the ions (cations and anions) located in the two compartments of the cell move with chlorides.

![](image)

**Fig. 2. Experimental arrangement of the electrodiffusion cell.**

We assume that the sample is saturated (convection neglected) and we define two types of electrolyte:

- Basic electrolyte: NaOH + KOH,
- Total electrolyte: NaOH + KOH + NaCl.

In the case of one-dimensional electrodiffusion, the current density due to the cations \((k)\), and the anions \((l)\) contained in the in the basic electrolyte are:

\[
i_P = -F \sum_{k=1}^{N} Z_k D_k \frac{\partial C_k}{\partial z} + \frac{E^2}{RT} \sum_{k=1}^{N} Z_k^2 D_k C_k \cdot E \tag{2}
\]

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\[ i_N = F \sum_{i=1}^{n} Z_i D_i \frac{\partial C_i}{\partial z} + \frac{F^2}{RT} \left( \sum_{i=1}^{n} Z_i^2 D_i C_i \right) E \]

Where:
- \( E \): Electrical field,
- \( R \): Gas constant,
- \( T \): The absolute temperature,
- \( F \): Faraday constant,
- \( D_k, D_l \): Diffusion coefficient of cations and anions respectively,
- \( C_k, C_l \): Cations and anions concentrations, respectively,
- \( Z_k, Z_l \): Cations and anions valence, respectively,
- \( Z \): The space variable.

The NaCl in the catholyte is decomposed to ions \( \text{Na}^+ \) and \( \text{Cl}^- \), generating current densities:

\[ i_{\text{Na}^+} = -FD_{\text{Na}^+} \frac{\partial C_{\text{Na}^+}}{\partial z} + \frac{F^2 D_{\text{Na}^+}}{RT} C_{\text{Na}^+} E \]  
\[ i_{\text{Cl}^-} = FD_{\text{Cl}^-} \frac{\partial C_{\text{Cl}^-}}{\partial z} + \frac{F^2 D_{\text{Cl}^-}}{RT} C_{\text{Cl}^-} E \]

In order to isolate the current \( i_{\text{Cl}^-} \) due solely to chloride transfer, we define:

\[ i_T = (i_p + i_{\text{Na}^+}) + (i_N + i_{\text{Cl}^-}) \]  
\[ i_T^* = (i_p + i_{\text{Na}^+}) - (i_N + i_{\text{Cl}^-}) \]

referred to current densities, total and conjugate, respectively.

We note:

\[ i_B = \gamma_B i_T \]  
\[ i_T = \gamma_T i_T \]

\( \gamma_B, \gamma_T \) represent the ratio between the current density and its conjugate for the basic and total electrolyte, respectively.

To take into account the electrical double layer, we introduce space charge densities \( \rho_B, \rho_S \) and conductivities \( \sigma_B, \sigma_S \) due to the basic electrolyte and to NaCl addition, respectively.
\[ \rho_B = F \left\{ \sum_{k=1}^{s} Z_k C_k - \sum_{l=1}^{p} Z_l C_l \right\} = F(C_p - C_N) \]  
\[ \rho_S = F(C_{Na^+} - C_{Cl^-}) \]  
\[ \sigma_B = \frac{F^2}{RT} \left\{ \sum_{k=1}^{s} Z_k^2 D_k C_k + \sum_{l=1}^{p} Z_l^2 D_l C_l \right\} = \frac{F^2}{RT} (\alpha_p D_p C_p + \alpha_N D_N C_N) \]  
\[ \sigma_S = \frac{F^2}{RT} (D_{Na^+} C_{Na^+} + D_{Cl^-} C_{Cl^-}) \]  

\( C_p, C_{Na^+}, \alpha_p, \alpha_N, D_p, D_N \) are defined in the appendix.

\( i_T \) and \( i_T^* \) become then:

\[ i_T = -D \left[ \frac{\partial \rho_B}{\partial z} + \rho \frac{\partial \sigma_B^*}{\partial z} + \lambda_S \left( \frac{\partial \rho_S}{\partial z} + \beta_S \frac{\partial \sigma_S^*}{\partial z} \right) \right] + D(\sigma_B^* + \lambda_S \sigma_S^*) E^* \]  
\[ i_T^* = -D \left[ \frac{\partial \sigma_B^*}{\partial z} \sigma_B^* + \lambda_S \frac{\partial \sigma_S^*}{\partial z} \right] + D(\rho_B + \beta_S \sigma_B^*) \lambda_S (\rho_S + \beta_S \sigma_S^*) E^* \]  

The parameters \( D, \beta, \beta_S, \sigma_B^*, \sigma_S^*, \lambda_S, E^* \) are defined in the appendix.

After defining local transfer equations, we establish macroscopic transfer equations at the porous medium scale [11] with the aim to determine the transfer current due solely to chlorides. Using the microstructural characteristics of the material, was carried out the transition from local transfer equations to macroscopic transfer equations: mainly the porosity and pore radius \( (R_{p_{max}}) \) corresponding to the peak in the pore size distribution. These properties have been obtained by Mercury Intrusion Porosimetry technique [12] (see experimental section). One notes by \([i]_B, [i]_T, [i]_B^*, [i]_T^* \) the macroscopic current densities and their conjugates in the basic and total electrolytes, respectively.

After theoretical developments, current densities are linked to conductivities by:

- for the basic electrolyte:

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\[
\frac{d \ln \sigma_B}{dz} = \left[ \frac{\gamma_B f_1(\sigma_B, z) - \beta f_2(\sigma_B, z)}{1 - \beta^2} \right]
\]

(12)

- for the total electrolyte:

\[
\frac{d \sigma_T}{dz} = \left[ \frac{\gamma_T f_1(\sigma_T, z) - \beta f_2(\sigma_T, z) + f_2(\sigma_S, z) - \beta f_1(\sigma_S, z)}{1 - \beta^2_T} \right] - \frac{\beta_T (\beta - \beta_S)}{(\sigma_B + \sigma_S)}
\]

(13)

Where:

\( f_1(\sigma_B, z) \) and \( f_2(\sigma_B, z) \) are defined in the appendix,

\( \sigma_s \) is the conductivity due to the NaCl addition, \( \sigma_s = \sigma_T - \sigma_B \), \( \sigma_T \) is the conductivity due to the total electrolyte.

Equations (12) and (13) are solved numerically by using Rung – Kutta method. In this resolution \( [i]_B \) and \( [i]_T \) are the inputs of the model, they are given by experiments (see next section). The parameters \( \gamma_B \) and \( \gamma_T \) are the outputs of the model.

From equation (6), the total macroscopic current density and its conjugate are:

- in the basic electrolyte:

\[
\begin{align*}
[i]_B & = i_p + i_N \\
[i^*]_B & = i_p - i_N
\end{align*}
\]

(14)

- after NaCl addition:

\[
\begin{align*}
[i]_T & = i_p + i_N + i_{Na^+} + i_{Cl^-} \\
[i^*]_T & = i_p - i_N + i_{Na^+} - i_{Cl^-}
\end{align*}
\]

(15)

From equations (7), (14) and (15), we have:

\[
i_{Cl^-} = \frac{(1 - \gamma_T) [i]_T - (1 - \gamma_B) [i]_B}{2}
\]

(16)

Flux and current density are linked by a proportionality relationship:

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\[ J_{CI} = \frac{i_{CI}}{Z_{CI}F} \]  \hspace{1cm} (17)

Then:

\[ J_{CI} = \frac{(1-\gamma_T)\mu F - (1-\gamma_B)\mu F}{2Z_{CI}F} \]  \hspace{1cm} (18)

3. Experimental study

3.1 Materials and specimens

Two types of materials were manufactured following a standardised procedure [13]: a cement mortar and a cement paste. The compositions of these materials and their microstructural characteristics are given in table 1.

The cement used was of type CEMI 42.5 according to European norm [14]. The specimens manufactured had a prismatic form (12×12×20 cm³). After being turned (24 hours after manufacturing), the specimens were immersed in an identical solution to that of the basic electrolyte of the electrodiffusion test (0.083 M of KOH and 0.025 M of NaOH). This immersion was maintained until the tests (90 days after specimens manufacturing). It allows us to reduce the leaching phenomena of the pore solution.

7 days after manufacturing, the samples tested in electrodiffusion (2 mortars and 2 pastes) were obtained by a technique of core sampling from the specimens with a prismatic form. This technique allows obtaining a homogeneous composition and avoiding the walls effects. The samples had a cylindrical form: diameter 7.5 cm; thickness 1.5 cm for mortar and 6.5 cm; 1 cm for paste.

The mercury intrusion porosimetry (MIP) test was carried out in order to quantify some parameters, which are needed for the model input, mainly the porosity and the pore radius \( R_{\text{pmax}} \).

Table 1: Characteristics of materials

<table>
<thead>
<tr>
<th>Material</th>
<th>C/S</th>
<th>W/C</th>
<th>Porosity (%)</th>
<th>( R_{\text{pmax}} ) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mortar</td>
<td>1/3</td>
<td>0.5</td>
<td>13.19</td>
<td>0.11</td>
</tr>
<tr>
<td>Paste</td>
<td>-</td>
<td>0.5</td>
<td>18.22</td>
<td>0.045</td>
</tr>
</tbody>
</table>

C: cement, S: sand, W: water

3.2 Electrodiffusion test

A classical cell was used (figure 2). The sample separates two compartments upstream (volume 2.10⁻³ m³) and downstream (volume 1.10⁻³ m³).

These compartments contained the identical basic electrolyte (0.083 M of KOH and 0.025 M of NaOH). The electrical field applied across the sample is of 300 V/m. This
value was chosen in order to reduce the Joule effect and the reactions at the electrodes [15].
The test starts with the basic electrolyte. It consists of a current monitoring in time (chronoamperometry). A renewal of the basic electrolyte is undertaken when the stationary current \( [I]_b \) is established. At the second renewal, the NaCl with concentration of 0.5 M is introduced in the upstream of the electrodiffusion cell. Concurrently to the current monitoring, a chloride dosage was carried out in the downstream compartment. For this, a selective electrode technique was used. The measured concentrations were then used to calculate an experimental flux by equation (19).
The steady state is reached when the total current \( [I]_T \) stabilises and the chloride concentration increase in the downstream compartment is linear. Then, the flux is constant and it is given by the relationship:

\[
J_{\text{exp}} = \frac{V_a \Delta C}{S \Delta t}
\]  

Where:
- \( V_a \): Volume of the anode cell,
- \( S \): Section of the sample,
- \( \Delta C \): Increase of the concentration in the course of the time interval \( \Delta t \).

4. Results and discussion

For lack of values of electrical double layer capacity \( C_{SH} \) in the literature, the value corresponding to silica is taken (3.73 x 10^{-5} F.m^{-2}). This value allows us to carry out the numerical resolution of transfer equations and consequently to know the parameters \( \gamma_B \) and \( \gamma_T \) on which the flux calculation is based. Calculations give for these parameters the following values:
- \( \gamma_B = -0.48 \) for mortar and paste,
- \( \gamma_T = -0.8 \) for mortar and -1.5 for paste.

Figures 3 and 4 show the evolution of the cumulated chloride concentration in time. For each material (mortar and paste), two migration tests were carried out. The experimental flux will be compared to the flux given by the model using current densities.
Fig. 3. Evolution of the cumulated chloride concentration in time for mortar.

Fig. 4. Evolution of the cumulated chloride concentration in time for cement paste.
The chronoamperometry carried out during the migration test allows us to record the evolution versus time of a global current density generated by the transfer of all chemical species contained in the cell. For our case, it concerns \( i_B \) due to ions \( \text{OH}^-\), \( \text{K}^+ \) and \( \text{Na}^+ \) with the basic electrolyte; and \( i_T \) due to the same ions with \( \text{Cl}^- \) (after NaCl addition). Figures 5 and 6 show the evolution of the current densities in time. The values of these two current densities when the steady state is reached are given in table 2.

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By using the values of $\gamma_B$ and $\gamma_T$ obtained by the numerical resolution of transfer equations and the experimental values of $[I]_B$ and $[I]_T$, the ‘theoretical’ flux for each sample is calculated by equation (18). These values and those of experimental flux are given in table 2.

Table 2. Experimental and calculated flux

<table>
<thead>
<tr>
<th>Samples</th>
<th>$[I]_B$ (Am$^{-2}$)</th>
<th>$[I]_T$ (Am$^{-2}$)</th>
<th>Calculated flux (Mm$^{-2}$s$^{-1}$) $\times 10^{-5}$</th>
<th>Experimental flux (Mm$^{-2}$s$^{-1}$) $\times 10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mortar 1</td>
<td>7.25</td>
<td>49.8</td>
<td>0.91</td>
<td>1.17</td>
</tr>
<tr>
<td>Mortar 2</td>
<td>7.4</td>
<td>5.7</td>
<td>0.36</td>
<td>1.11</td>
</tr>
<tr>
<td>Paste 1</td>
<td>23.9</td>
<td>12.6</td>
<td>4.29</td>
<td>7.84</td>
</tr>
<tr>
<td>Paste 2</td>
<td>22.9</td>
<td>12.1</td>
<td>4.08</td>
<td>6.35</td>
</tr>
</tbody>
</table>

The comparison of experimental flux and those calculated by the model (Table 2) shows that the two values of flux calculated and measured are of the same order of magnitude for all the samples tested. However, direct measurements of electrical double layer capacity will allow a better adjustment of the parameters $\gamma_B$ and $\gamma_T$ given by the numerical resolution. One will thus obtain "theoretical" flux even closer to experimental flux based on the chlorides dosage in downstream of electrodiffusion cell.

In addition, whatever the method chosen, this dosage at the downstream requires a heavier experimental procedure and consequently less precise than a follow-up of the evolution of electrical current according to time. Here lies interest of this work.

As it is shown in figures 5 and 6, currents decrease after NaCl addition. We explain this phenomenon by the establishing of the electrical double layer. One of its effects would be to slow down the chloride transfer (i.e. the current density), by the electrocapillary phenomena that it engenders (Fig. 1).

5. Conclusion

We propose in this work a new method for chloride flux calculating during migration test in cementitious materials. We showed that chronoamperometry is enough to calculate the chloride flux. Thus, one avoids chloride titration, which is a heavy operation and time consuming.

In addition, quantifying the effect of electrical double layer, which occurs between the pore solution and the pore walls, allows us to get a more complete analysis of this type of transfer. This effect is expressed by the double layer capacity $C_{dH}$ that can be found in the functions $f_1(\sigma, z)$, $f_2(\sigma, z)$ through the parameter $\mu$. However, it remains desirable to solve transfer equations in transitory regime, in order to integrate temporal evolution of transfer, and therefore of the flux.

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Furthermore, this work would be completed by a consistent experimental study on different compositions of cement-based materials in order to reinforce these first conclusions.

Appendix

\[ f_1(\sigma, z) = \frac{\sigma + \lambda_c \left[ \sqrt{z^2 + 4\mu^2\sigma} - 2\mu \sigma^{1/2} \right]}{\left[ \sigma + \lambda_c \left( \sqrt{z^2 + 4\mu^2\sigma} - 2\mu \sigma^{1/2} \right)^2 - \lambda_c^2 z^2 \right]} \]

\[ f_2(\sigma, z) = \frac{\lambda_c z}{\left[ \sigma + \lambda_c \left( \sqrt{z^2 + 4\mu^2\sigma} - 2\mu \sigma^{1/2} \right)^2 - \lambda_c^2 z^2 \right]} \]

where: \( \sigma \) can take value of \( \sigma_B \) or that of \( \sigma_S \).

\[ \lambda_S = \frac{D_N}{D} \quad \beta = \frac{\alpha_p D_p - \alpha_N D_N}{\alpha_p D_p + \alpha_N D_N} \]

\[ D = \frac{(\alpha_p + \alpha_N) D_p D_N}{\alpha_p D_p + \alpha_N D_N} \quad D_S = \frac{2D_N a - D_C}{D_N a + D_C} \]

\[ \alpha_p = \frac{\sum_{k=1}^{s} Z_k^2 D_k C_k}{D_p C_p} \quad \alpha_N = \frac{\sum_{l=1}^{p} Z_l^2 D_l C_l}{D_N C_N} \]

\[ E^* = \frac{F}{RT} E \quad \sigma_B^* = \frac{RT}{FD} \sigma_B \]

\[ \beta_S = \frac{D_N a - D_C}{D_N a + D_C} \quad \mu = \frac{(1 - \beta^2) \sigma_B \delta_0}{C_{SH} EL} \]

\[ \lambda_c = \frac{\tau_C}{\chi} \quad \chi = \frac{RT}{FE L} \quad \beta_T = \frac{D_{PS} - D_{NS}}{D_{PS} + D_{NS}} \]

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\[ D_{PS} = \frac{D_p C_p + D_{Na^+} C_{Na^+}}{C_p + C_{Na^+}} \]
\[ D_{NS} = \frac{D_N C_N + D_{Cl^-} C_{Cl^-}}{C_N + C_{Cl^-}} \]

- \( C_p \): concentration of anions (M)
- \( C_p \): concentration of cations (M)
- \( C_{SII} \): equivalent capacity of electrical double layer (F m\(^{-2}\))
- \( D \): global equivalent ionic diffusion coefficient before NaCl addition (m\(^2\) s\(^{-1}\))
- \( D_s \): equivalent ionic diffusion coefficient of sodium and chloride (m\(^2\) s\(^{-1}\))
- \( E \): applied electrical field (V m\(^{-1}\))
- \( L \): sample thickness (m)
- \( \alpha_p, \alpha_N \): equivalent valence of ionic transfer for cations and anions, respectively
- \( \beta \): coefficient that represents the gap between diffusion coefficients of ions contained in the basic electrolyte
- \( \beta_s \): coefficient that represents the gap between diffusion coefficients Na\(^+\) and Cl\(^-\)
- \( \delta_0 \): thickness of electrical double layer (m)
- \( \tau_C \): time constant that characterises the adsorption electrocapillary phenomena (s)
- \( \tau_D \): time constant that characterises the diffusion process (s)

References


13. European norms, EN 196-1, Méthodes d’essais des ciments.


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