Problems associated with the measurement of chloride diffusion in concrete

Peter Claisse and Juan Lizarazo Marriaga, Coventry University, Priory Street, Coventry CV1 5FB, UK

Presentation contents
1. Electromigration tests
2. “Traditional” diffusion tests
ASTM C1202 – Names for the Test

• Standard Test Method for Electrical Indication of Concrete’s Ability to Resist Chloride Ion Penetration (in the ASTM).
• The Rapid Chloride Permeability Test (after Whiting – who invented the test)
• The Coulomb Test (it measures Coulombs)
ASTM C1202: Rapid Chloride Penetration Test (RCPT)

Mesh electrodes

Concrete sample

Solid acrylic cell

Reservoir 0.3N NaOH

Reservoir 3% NaCl

Coating

Charge Passed (coulombs)

<table>
<thead>
<tr>
<th>Charge Passed (coulombs)</th>
<th>Chloride Ion Penetrability</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;4,000</td>
<td>High</td>
</tr>
<tr>
<td>2,000 - 4,000</td>
<td>Moderate</td>
</tr>
<tr>
<td>1,000 – 2,000</td>
<td>Low</td>
</tr>
<tr>
<td>100 – 1,000</td>
<td>Very low</td>
</tr>
<tr>
<td>&lt;100</td>
<td>Negligible</td>
</tr>
</tbody>
</table>
The Problem

- At the start of the test there is no chloride in the sample so the current depends on other charge carriers (primarily OH-)
- Adding pozzolans to concrete depletes the OH-
- Thus pozzolanic mixes can give misleading results
The new test

- D.C. power supply
- Capillary pipe / salt bridge
- KCl solution
- Reservoir - NaCl
- Reservoir - NaOH
- Concrete sample
- Coating
- Mesh electrodes
- Solid acrylic cell
- Potential difference cathode and sample mid point
- Reference electrode SCE
Using the mid-point voltage to identify cement replacements
Electro-diffusion model for chlorides in concrete

- Nernst-Planck equation:

\[
J_i = D_i \frac{\partial c_i}{\partial x} + \frac{z_i F}{RT} D_i c_i \frac{\partial E}{\partial x}
\]

- Charge electroneutrality (Kirchoff’s law):

\[
0 = F \sum_i z_i J_i
\]
Solving the hard way –

assuming E is constant

\[ I = FADc_0a\left[\frac{2}{\beta\sqrt{\pi}}\right]\left(\frac{\alpha - \alpha^2}{\beta^2 - 16}\right) + \frac{1}{2}\text{erfc}\left(\frac{\alpha}{\beta} - \frac{\beta}{4}\right) \]

where

\[ a = \frac{zFE}{RT} \]

\[ \alpha = ax \]

\[ \beta = 2a\sqrt{Dt} \]
Section through sample during test

Chloride zone  Sodium zone
Low resistance (high D)  High resistance (low D)

Electrostatic field $E$ is gradient
Membrane Potential

Diagram showing the distribution of ions across a membrane, including Na+, Cl-, Na+, OH-, K+, 2OH-, Ca+, and OH-. The diagram illustrates the relationship between external voltage, membrane potential, and distance.

Key elements:
- External voltage
- Membrane potential
- Na+, Cl-, Na+, OH-, K+, 2OH-, Ca+, OH-

Graph showing the voltage and distance relationship with external voltage.
Modelling a thin slice of the sample for a short time step

Apply Kirchoff’s law: current in = current out

Electromigration into element - set by field E which was calculated for the last element

Diffusion in and out – fixed by concentration gradient

Electromigration out of element – we can set this for charge neutrality by adjusting the field E

Final adjustments are needed to get the correct total voltage across the sample.
Key innovation in the computer code

INPUTS

Set linear voltage drop for all space steps

Calculate diffusion flux for each ion in all space steps

Calculate electro-migration flux for each ion in all space steps

Is there total charge surplus in any space step?

Reach time limit?

Correct the voltage in all space steps to prevent charge build up MEMBRANE POTENTIAL
Current in amps at different times in hours vs position in mm from the negative side

**Time = 0**

- Potassium
- Sodium
- Chloride
- Hydroxyl

**Time = 7**

- Potassium
- Sodium
- Chloride
- Hydroxyl

**Time = 14**

- Potassium
- Sodium
- Chloride
- Hydroxyl
Model output for current and voltage

Current vs time with no voltage correction (average)

Voltage adjustments at different times
Transport properties

- Intrinsic diffusion coefficient (Cl⁻)
- Intrinsic diffusion coefficient (OH⁻)
- Intrinsic diffusion coefficient (Na⁺)
- Intrinsic diffusion coefficient (K⁺)
- Porosity (ε)
- Chloride binding capacity factor (α)
- OH⁻ conc. of the pore solution

Optimization Model

Electro-diffusion model: 
Voltage control

Data base

Artificial Neural Network

Network training

Experiments
- Current
- Membrane potential
## Experimental programme

<table>
<thead>
<tr>
<th>Mix</th>
<th>w/b</th>
<th>OPC %</th>
<th>PFA %</th>
<th>GGBS %</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>0.49</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30% PFA</td>
<td>0.49</td>
<td>70</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>50% GGBS</td>
<td>0.49</td>
<td>50</td>
<td>0</td>
<td>50</td>
</tr>
</tbody>
</table>

**Inputs of the neural network**

![Graph 1: Membrane potential vs. time](image1.png)

![Graph 2: Current vs. time](image2.png)
Chloride related properties from voltage control model
You can’t get this lot with the new 5 minute test!
“Traditional” diffusion test

For modelling:

• The boundary condition is not zero voltage because the ends of the sample are not short-circuited.
• A voltage can be measured.
• The voltage in the model is set to give zero current.
Equation (7) is the integral of Fick’s law. $D_{\text{intr}} = \text{Intrinsic diffusion coefficient}$

(3) and (4) coincide – showing that the computer model gives the same results as integrating Fick’s law if the ion-ion interactions are switched off.

(5) Is based on experimental data
Future work

• Controlled power tests to avoid overheating.

• Voltage steps to avoid the need for a salt bridge.
Conclusions

• The electrical model can be used with an artificial neural network (ANN) to give good values for transport properties.

• Even when no voltage is applied, an electrical model is needed to simulate a diffusion test because of ion-ion interactions.
Thank you
www.claisse.info

References:

J Lizarazo Marriaga and P Claisse
Effect of non-linear membrane potential on the migration of ionic species in concrete

Juan Lizarazo-Marriaga, Peter Claisse
Determination of the concrete chloride diffusion coefficient based on an electrochemical test and an optimization model

J Lizarazo and P Claisse
Determination of the transport properties of a blended concrete from its electrical properties measured during a migration test
Submitted to Magazine of Concrete Research. September 08.

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June 28 - June 30, 2010, Università Politecnica delle Marche, Ancona, Italy.
http://www4.uwm.edu/cbu/ancona.html