Problems associated with the measurement of chloride diffusion in concrete

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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)

Reservoir 0.3N NaOH
Concrete sample
Mesh electrodes
Solid acrylic cell
Coating

Reservoir 3% NaCl

Charge Passed (coulombs) | Chloride Ion Penetrability
---|---
>4,000 | High
2,000 - 4,000 | Moderate
1,000 - 2,000 | Low
100 - 1,000 | Very low
<100 | Negligible
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- and can give misleading low results.
• Adding some accelerators with nitrates or other conducting ions can give misleading high results.
The new test

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

• Nernst-Planck equation:

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

Diffusion  Migration

• Charge electroneutrality (Kirchoff’s law):

\[ 0 = F \sum_i z_i J_i \]
Solving the hard way –
assuming E is constant

\[ I = FADc_o a \left[ \frac{2}{\beta \sqrt{\pi}} e^{\frac{\alpha}{2} \frac{\alpha^2}{\beta^2} \frac{\beta^2}{16}} \right] \]

\[ + \frac{1}{2} \text{erfc}\left(\frac{\alpha}{\beta} - \frac{\beta}{4}\right) \]

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
The Progress of a Chloride Ion

A Chloride ion enters the sample... what happens next?

Either it finds another negative ion that can move away in front of it

Or it has to bring a positive sodium ion with it
Na$^+$
Cl$^-$

External voltage

Na$^+$
OH$^-$
K$^+$
OH$^-$
Ca$^+$
2OH$^-$

OH$^-$
Na$^+$

Voltage

Membrane potential

External voltage

Distance
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?

Correct the voltage in all space steps to prevent charge build up

MEMBRANE POTENTIAL

Increase time

Reach time limit?

No

Yes
Current in amps at different times in hours vs position in mm from the negative side

Time = 0

Time = 7

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
Optimization Model

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

Electro-diffusion model: Voltage control

Artificial Neural Network

Data base

Experiments
- Current
- Membrane potential

Network training
Experimental programme

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<th>Mix</th>
<th>w/b</th>
<th>OPC %</th>
<th>PFA %</th>
<th>GGBS %</th>
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<td>50%GGBS</td>
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</tbody>
</table>

- **Mix w/b**: OPC 0.49, 30%PFA 0.49, 50%GGBS 0.49
- **OPC %**: 100, 70, 50
- **PFA %**: 0, 30, 0
- **GGBS %**: 0, 50, 50

**Inputs of the neural network**
Chloride related properties from voltage control model. You can’t get these with a 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.
Traditional diffusion test (no applied voltage)

Equation (7) is the integral of Fick’s law. $D_{\text{int}} = \text{Intrinsic diffusion coefficient}$

(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 on the Voltage Driven Test

• Controlled power tests to avoid overheating.

• Voltage steps (or similar technique) to get the same results but 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:

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http://www4.uwm.edu/cbu/ancona.html