Transport properties of concrete: measurement and applications
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Presentation slides deposited in CURVE May 2014

Original citation & hyperlink:

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Transport Properties of Concrete: Measurement and applications

Professor Peter A Claisse
Coventry University, Coventry UK
Transport Properties of Concrete: Measurement and applications

- The transport processes
  - Pressure driven flow
  - Diffusion,
  - Electromigration
  - Thermal migration

- Processes which promote or inhibit transport
- Surface permeability tests
- Electrical tests
- Application of the results
Pressure driven flow (permeation or advection)

- Water (which may contain salt) flows in the direction of the applied pressure.
- The flux $F$ depends on the pressure gradient $\frac{dP}{dx}$
  
  $F = \frac{KA}{e} \frac{dP}{dx}$ \text{ m}^3/\text{s}$

- $K = \text{permeability}$
- $A = \text{Area}$
- $E = \text{viscosity}$
Diffusion

When the salt dissolves into the water it will assume an equal concentration at all points throughout the liquid and will enter the concrete. The flux depends on the concentration gradient $dC/dx$

$$F = D \frac{dC}{dx} \text{ kg/m}^2/\text{s}$$

$D =$ diffusion coefficient
Electromigration

The flux depends on the electrostatic field $E$ i.e. the voltage gradient (Volts/m)

$$F = \frac{DzECF}{RT}$$

$Z = \text{valence}, R = \text{gas constant}, T = \text{temperature}$

Solution with supply of negative ions

Negative ions, e.g. chloride

Solution with supply of positive ions

Positive ions
Thermal Gradient

A concrete structure which has been contaminated with de-icing salt heats up in sunlight

Hot (fast moving) particles

Cold (slow moving) particles
Transport Properties of Concrete: Measurement and applications

- The transport processes
- Processes which promote or inhibit transport
  - Adsorption (inhibits)
  - Capillary suction (promotes)
  - Osmosis (promotes)
- Surface permeability tests
- Electrical tests
- Application of the results
Adsorption

Adsorbed ions are fixed into the matrix in various ways and are unable to move and therefore unable to cause any deterioration.

The ratio of total concentration (including adsorbed ions) to concentration in solution is the “capacity factor”.
Definitions

\[ \alpha = \frac{C_s}{C_l} \]

\( C_1 \): free ions per unit volume of liquid (pore solution)

\( C_s \): total ions per unit volume of the solid (concrete)

\( \alpha \): capacity factor

\( \varepsilon \): porosity

The flux is calculated per unit area of the porous material (concrete) and the average concentration in the concrete

\[ F = D_{app} \frac{dC_s}{dx} \]

The flux is calculated per unit cross-sectional area of the pores and the concentration in the pore solution

\[ F = \varepsilon . D_i \frac{dC_l}{dx} \]

\[ \frac{\alpha}{\varepsilon} = \frac{D_i}{D_{app}} \]
The effect of adsorption
(Calculations from a computer model).

![Graph showing breakthrough time vs. capacity factor with data points for Base case and Diffusion Control.]
Capillary Suction

Water rises up a small diameter glass capillary tube to a height $h$

$$h = \frac{2s}{r \rho g} \text{ m}$$

$s =$ surface tension
$r =$ pore radius
$\rho =$ density
$g =$ gravitational constant
Osmosis

Solution with high salt concentration

Concrete

Solution with low salt concentration
Transport Properties of Concrete: Measurement and applications

- The transport processes
- Processes which promote or inhibit transport
- **Surface permeability tests**
  - Tests using water
  - Tests using a vacuum
- Electrical tests
- Application of the results
Surface tests using water
ISAT and Cover Concrete test

Reservoir in funnel
Glass capillary fixed to ruler
Plastic pipe
Perspex cap
Concrete sample

Reservoir in funnel
Glass capillary fixed to ruler
Inlet pipe
Tap
Rubber seal
Concrete sample

50mm
13mm
ISAT apparatus

Reservoir

Glass capillary

Tap

Perspex cap

Sample
Surface tests using vacuum
Air Permeability Near Surface
and Figg tests

To vacuum pump

To pressure gauge

Concrete sample

Perspex cap

Hypodermic needle

Silicone plug

Concrete sample

Tap

20mm

30mm

13mm
Effect of humidity on gas permeability

Permeability * $10^{-21} \text{ m}^2$

Hydrogen  Helium  Methane  Argon  Carbon dioxide

Dry  75% RH  100% RH
Vacuum Preconditioning

Vacuum applied until silica gel turns blue

Concrete sample

Perspex cap

To vacuum pump

Tap

Vacuum

2 day

Oven (105 deg C)

Twice vacuum

ISA at 10 minutes *10^-2 ml/m^2/s

<table>
<thead>
<tr>
<th>60 N/mm² water curing</th>
<th>35 N/mm² water curing</th>
<th>60 N/mm² air curing</th>
<th>35 N/mm² air curing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>60 N/mm² air curing</td>
<td>35 N/mm² air curing</td>
<td>60 N/mm² air curing</td>
</tr>
<tr>
<td>2 day</td>
<td>35 N/mm² air curing</td>
<td>60 N/mm² air curing</td>
<td>35 N/mm² air curing</td>
</tr>
<tr>
<td>Oven (105 deg C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Twice vacuum</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Choosing a test

- The water tests are more sensitive to concrete permeability than the gas tests.
- No clear advantage of either drilled hole or surface tests.
- The tests measure different properties in that the water tests measure capillary suction as well as permeability.
- If possible, a site test programme should use more than one test.
Analytical solutions for the tests

- ISAT
  \[ F = A \left( \frac{Ks\varepsilon}{re} \right)^{\frac{1}{2}} t^{-\frac{1}{2}} \]

- The permeability K can be calculated

\[ K = \frac{e x_0^2}{\ln \left( \frac{(55 \times 10^3 + P_a) (45 \times 10^3 - P_a)}{(55 \times 10^3 - P_a) (45 \times 10^3 + P_a)} \right)} \]

- Figg

\[ 2P_d \Delta t \left[ \frac{1}{\ln \left( \frac{X}{x_0} \right)} - \frac{1}{L} \left( \frac{1}{X} - \frac{1}{x_0} \right) \right] \]

- The permeability cannot be calculated without knowing the distance X over which the pressure drops
Measuring gas permeability requires more than one hole in the concrete sample with sealed tops and voids below.

Apply a vacuum to the centre hole and monitor the pressure in the side holes.

To gauge  To vacuum  To gauge
The Klinkenberg equation:
At low pressures gas permeability varies with pressure

\[ K_l = \frac{K_g}{\left(1 + \frac{b}{P_m}\right)} \]

- \( K_l \) = Water intrinsic permeability of concrete
- \( K_g \) = Gas intrinsic permeability of concrete
- \( P_m \) = The mean pressure at which gas is flowing

The graph shows the relationship between permeability and average pressure in atmospheres.
Comparison of permeabilities

- Water Permeability from High Pressure m²
- Average permeability from ISAT m²
- Calculated water permeability from Klinkenberg equation
- Line of equality

Graph showing comparison of gas permeability from three-hole test m² against water permeability m².
Transport Properties of Concrete: Measurement and applications

• The transport processes
• Processes which promote or inhibit transport
• Surface permeability tests
• Electrical tests
  – The “Rapid Chloride test”
  – Modelling ion-ion interactions
  – The Nordtest
  – Simple diffusion test (current control)
• Application of the results
ASTM C1202: Rapid Chloride Penetration Test (RCPT)

Mesh electrodes

60 V

Concrete sample

Reservoir 0.3N NaOH

Reservoir 3% NaCl

Coating

Solid acrylic cell

<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 insitu version of the rapid chloride test

- Sodium chloride
  - 0 Volts

Cover concrete → Chloride ions → Reinforcing bar

+60 volts
Current is measured
Solving the hard way –

assuming E is constant

\[ i = A F D_{cl} c_s \left[ \frac{1}{\sqrt{\pi D_{cl} t}} e^{\frac{(x-aD_{cl} t)^2}{4D_{cl} t}} + \frac{a}{2} \text{erfc} \left( \frac{x - aD_{cl} t}{2\sqrt{Dt}} \right) \right] \]

Where \( a = \frac{zFE}{RT} \)

This gives a solution for diffusion and electromigration of a single ion but it takes no account of ion-ion interactions so computer modelling must be used.
The Progress of a Chloride Ion

Cl- – – – – – – – – – – – – –
A Chloride ion enters the sample... what happens next?

Cl- – – – – – – – – – – – – –
OH- – – – – – – – – – – – – –
Either the ion is adsorbed – forms chloroaluminate.

Cl- – – – – – – – – – – – – –
OH- – – – – – – – – – – – – –
or it stops because the concentration gradient falls making it less mobile than the OH-

Cl- – – – – – – – – – – – – –
Cl- – – – – – – – – – – – – –
or it carries on...
Section through sample during test

Chloride zone
Low resistance (high D)

Sodium zone
High resistance (low D)

Electrostatic field
$E$ is gradient

Voltage
Membrane Potential

External voltage

\[ \text{Na}^+ \quad \text{Cl}^- \]

\[ \text{Na}^+ \quad \text{OH}^- \quad \text{K}^+ \quad 2\text{OH}^- \quad \text{Ca}^+ \]

\[ \text{OH}^- \quad \text{Na}^+ \]

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.
Electro-diffusion model for chlorides

- **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 \quad Migration

- **Charge electroneutrality (Kirchoff’s law):**
  \[ 0 = F \sum_{i} z_i J_i \]
Key elements of 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?

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

No

Reach time limit?

Increase time
Checking the model – Salt bridge measurements

- 4 mm drilled hole
- small bore pipe
- Reference electrode (connected to data logger)
- Potassium chloride
Salt Bridge Apparatus

- Reference electrode SCE
- Capillary pipe / salt bridge
- KCl solution
- Reservoir - NaCl
- Reservoir - NaOH
- Concrete sample
- Mesh electrodes
- Solid acrylic cell
- Coating
- Potential difference cathode and sample mid point
- D.C. power supply

Photos:
- 02/08/2008
Results from salt bridge

Membrane Potential: $\Delta V = V_n - V_0$

Experimental data
Model output for current and voltage

Current vs time with no voltage correction (average)
Concentrations in cells at distances from negative side in mol/m³ vs time in hours

**Hydroxyl**

- **Negative**
- **Positive**

**Potassium**

- **Negative**
- **Positive**

**Sodium**

- **Negative**
- **Positive**

**Chloride**

- **Negative**
- **Positive**
Current in amps at different times in hours vs position in mm from the negative side
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

Data base
- Electro-diffusion model: Voltage control
- Artificial Neural Network

Experiments
- Current
- Membrane potential

Network training
Artificial Neural Network

Input layer

- M.P. Membrane potential at 1.2 hours
- M.P. Membrane potential at 3.6 hours
- M.P. Membrane potential at 6 hours
- Current at start
- Current at 3.6 hours
- Current at 6 hours

Output layer

- OH pore concentration
- Cl diffusion coefficient
- OH diffusion coefficient
- Na diffusion coefficient
- K diffusion coefficient
- Capacity factor of Cl binding
- Porosity
Chloride related properties from experimental data used in the model

**Diffusion Coefficients**

- **Coefficient of diffusion [m²/s]**
- **Options:** Dapp CL, Dapp OH, Dapp Na, Dapp K
- **Values:**
  - OPC: 0.179
  - 30 FA: 0.169
  - 50 GGBS: 0.167

**Porosity**

- **Values:**
  - OPC: 0.179
  - 30 FA: 0.169
  - 50 GGBS: 0.167

**CI capacity factor**

- **Values:**
  - OPC: 0.36
  - 30 FA: 0.39
  - 50 GGBS: 0.40

**OH Concentration [mol/m³]**

- **Values:**
  - OPC: 262.0
  - 30 FA: 166.8
  - 50 GGBS: 154.8
Comparing different mixes in the rapid chloride test.
Membrane potential (left) and current vs. time (right)
How to get more from the rapid chloride test

• Measure the mid-point voltage
• Measure the initial and final current as well as the average
• Run for as long as possible
• Keep the reservoirs small so they get depleted.
The Nordtest NT Build-492 Test

- Rubber sleeve
- Anolyte
- Stainless steel anode
- Sample
- Catholyte
- Stainless steel Cathode
- Support
- Plastic Box
Modelling the Nordtest without ion-ion interactions (left) and with ion-ion interactions (right)
“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.
Voltage control model

- External voltage: fixed (≠0)
- Membrane potential: calculated (≠0)
- Total current: calculated (≠0)

Migration test

Total current

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Current A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>2.5</td>
</tr>
<tr>
<td>0.200</td>
<td>7.5</td>
</tr>
<tr>
<td>0.400</td>
<td>12.5</td>
</tr>
<tr>
<td>0.600</td>
<td>17.5</td>
</tr>
<tr>
<td>0.800</td>
<td>22.5</td>
</tr>
<tr>
<td>1.000</td>
<td>27.5</td>
</tr>
<tr>
<td>1.200</td>
<td>32.5</td>
</tr>
<tr>
<td>1.400</td>
<td>37.5</td>
</tr>
<tr>
<td>1.600</td>
<td>42.5</td>
</tr>
<tr>
<td>1.800</td>
<td>47.5</td>
</tr>
</tbody>
</table>

Legend:
- Yellow: hydroxyl
- Purple: chloride
- Red: sodium
- Green: potassium
Current control model (I)

- External current: fixed (≠0)
- Membrane potential: calculated (≠0)
- Required voltage: calculated (≠0)

\[ \text{Total current} \]

\[ \begin{array}{cccccccc}
0.000 & 0.020 & 0.040 & 0.060 & 0.080 & 0.100 & 0.120 \\
2.5 & 12.5 & 22.5 & 32.5 & 42.5
\end{array} \]

\[ \text{Current A} \]

\[ \text{Distance mm} \]

- Cathodic protection
- Electrochemical extraction

\[ \text{hydroxyl} \]
\[ \text{sodium} \]
\[ \text{chloride} \]
\[ \text{potassium} \]
Current control model (II)

- External current: fixed (\(=0\))
- Required voltage equal to membrane potential (\(\neq 0\))

Self diffusion

![Graph showing total current over time with different ion contributions at various distances.](image-url)
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
Comparing simple diffusion with the rapid chloride test.

![Graph showing chloride % of cementitious in drilled hole test for Silica Fume and CEM1]
Selecting an electrical test

• All measurements of diffusion in concrete, with or without applied voltages, are significantly affected by ion-ion interactions.

• For the comparison of mixes with different cementitious materials in them a simple diffusion test should be used unless computer modelling is used to correct the results of electrical tests.

• The electrical tests are suitable for quality control purposes.

• For modelling the life of structures a diffusion coefficient which includes some “adjustment” for ion-ion interactions (such as that obtained by applying Fick’s law to a simple diffusion test) should be used.
Transport Properties of Concrete: Measurement and applications

- The transport processes
- Processes which promote or inhibit transport
- Surface permeability tests
- Electrical tests

• Application of the results
  – Durability
  – Waste containment
## Factors Affecting Durability

<table>
<thead>
<tr>
<th>Factors which can be controlled</th>
<th>Properties of the matrix</th>
<th>Transport Processes</th>
<th>Deterioration Processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water to cement ratio</td>
<td>Hydrate Structure</td>
<td>Pressure driven flow</td>
<td>Freeze-Thaw</td>
</tr>
<tr>
<td></td>
<td>Pore interconnection (formation factor)</td>
<td>Diffusion</td>
<td>Sulphate Attack</td>
</tr>
<tr>
<td>Curing conditions</td>
<td>Porosity (total pore volume)</td>
<td>Electromigration</td>
<td>Alkali-silica reaction</td>
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<tr>
<td>Environmental conditions</td>
<td>Pore fluid content</td>
<td>Thermal Gradient</td>
<td>Reinforcement Corrosion</td>
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<tr>
<td>Degree of compaction</td>
<td>Pore fluid chemistry</td>
<td>Osmosis</td>
<td>Salt Crystallisation</td>
</tr>
<tr>
<td>Cement Type</td>
<td>Matrix chemistry</td>
<td>Capillary suction</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adsorption</td>
<td></td>
</tr>
</tbody>
</table>
Effect on corrosion current

- Silica fume in curing
- Portland cement in curing
- Silica fume in chloride
- Portland cement in chloride

Graph showing the change in lag corrosion current (Amps) for various factors:
- Carbonation strain
- Chloride in gravity test
- Log oxygen permeability
- Compressive strength
- Carbonation depth at 18 days
- Carbonation depth at 28 days
- Electrical conductivity
- Lime content
- Water vapour transport
Novel landfill barrier. Transport with advection and diffusion

**Composition**

- Alkali activated slag or pozzolan concrete containing spent foundry sand and metallurgical slag aggregate
- Non-swelling clay or “artificial clay”.
- Concrete containing aggregate of larger particles of metallurgical slag and waste and spent foundry sand.

**Main Physical Function**

- Mechanical support of vehicles during operational phase and initial containment of leachate
- Physical containment of leachate and crack sealing.
- Chemical conditioning of leachate to promote adsorption and physical containment with low permeability and diffusion coefficient. Base for sealing layer.
Comparing the model with a site trial

![Graph showing comparison between model and experimental data for Ca cell 2. The graph plots Cl ppm against Time years. The model data is represented by dots, and the experimental data is represented by crosses and triangles.]

- Model top of clay
- Model bottom of clay
- Experimental top of clay
- Experimental bottom of clay
Conclusions

• The fundamental transport equations may be applied with either analytical solutions or computer models. The computer models are more versatile.

• Modelling indicates that water tests are better than vacuum tests for surface measurement.

• The rapid chloride test should only be used with modelling of ion-ion interactions.

• Transport modelling is an effective tool for waste containment modelling.
Thank you
www.claisse.info

Coventry University and
The University of Wisconsin Milwaukee Centre for By-products Utilization
Third International Conference on
Sustainable Construction Materials and Technologies
Kyoto, Japan, August 18-21, 2013. See: www.scmt.org.uk