Concrete Degradation Modeling Research at NIST

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Similarities to Other Models

- Chemistry of the pore solution
- Dissolution/Precipitation reactions
- Empirical porosity dependence of transport coeff.
- Physics and chemistry treated separately
- Chemical reaction is a boundary condition to transport

Uniqueness at NIST

Modeling concentrated electrolytes

- Activity coefficients: Pitzer
- Solution density: y/γ
- Solution viscosity: D(c)
- Equivalent conductivity: u(c)

Validation Approach

- Binary/ternary diffusion coefficient
- Solution conductivity
- Transference number
- Diffusion potential

Parameter-free calculations!

Electrolyte

Electro-Diffusive flux:

$$\mathbf{j}_i = -\frac{D_i}{RT} c_i \nabla \mu_i - z_i u_i c_i \nabla \psi \qquad \mu_i = \mu_i^\circ + RT \ln y_i c_i$$

Electroneutrality:

$$F \sum_i z_i \mathbf{j}_i = 0$$

Electrical Field:

$$\mathbf{E} = -\nabla \psi = \frac{\frac{F}{RT} \sum_i z_i D_i c_i \nabla \mu_i}{\sum_i z_i^2 F u_i c_i}$$

Implementation Details

$$\mathbf{j}_i = -\frac{D_i}{RT}\, c_i \nabla \mu_i - z_i u_i c_i \nabla \psi$$

Diffusion Coefficient:

$$D_i = D_i^s \left(\frac{\eta_w}{\eta_{soln}} \right)^{1.0}$$

Viscosity:

$$\left(\frac{\eta_{soln}}{\eta_w} \right) = 1 + \sum_i A_i\, c_i^{1/2} + B_i\, c_i$$

Implementation Details

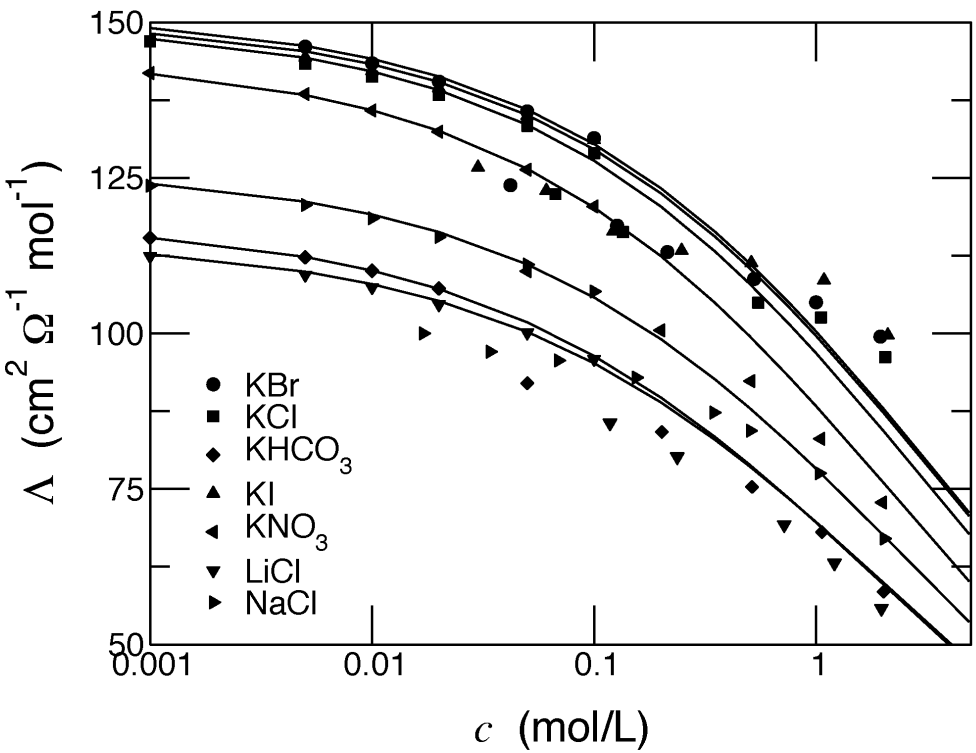
$$\mathbf{j}_i = -\frac{D_i}{RT}\, c_i \nabla \mu_i - z_i u_i c_i \nabla \psi$$

Electrochemical Mobility:

$$\Lambda = \sum_i \lambda_i \qquad \lambda_i = F\, u_i \qquad \lambda_i = \frac{\lambda_i^o}{1 + G_i\, I_c^{1/2}}$$

Conductivity:

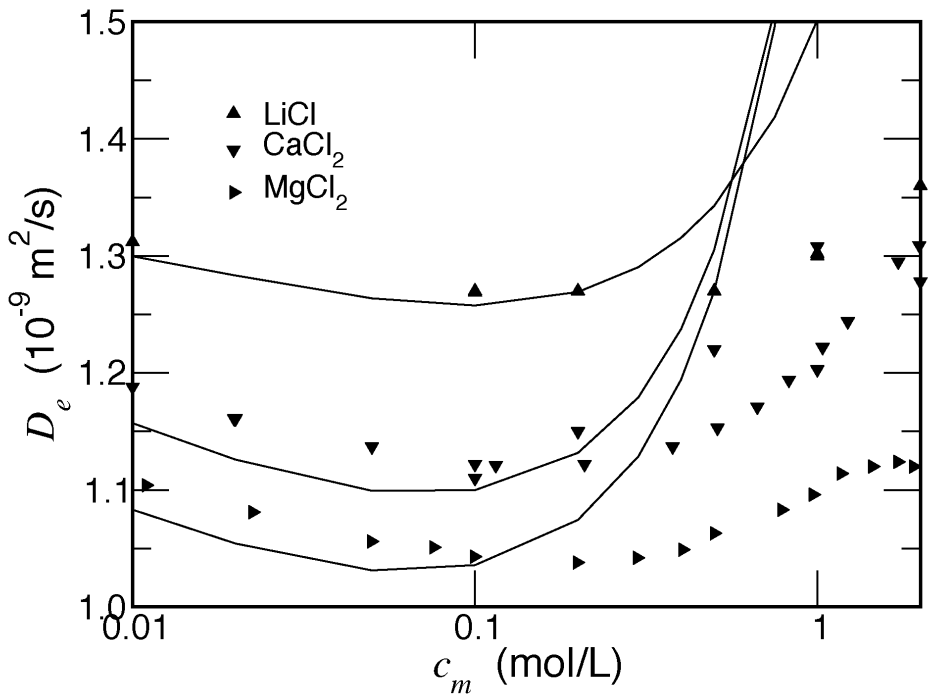
$$\sigma = \sum_i z_i^2\, c_i\, \lambda_i$$

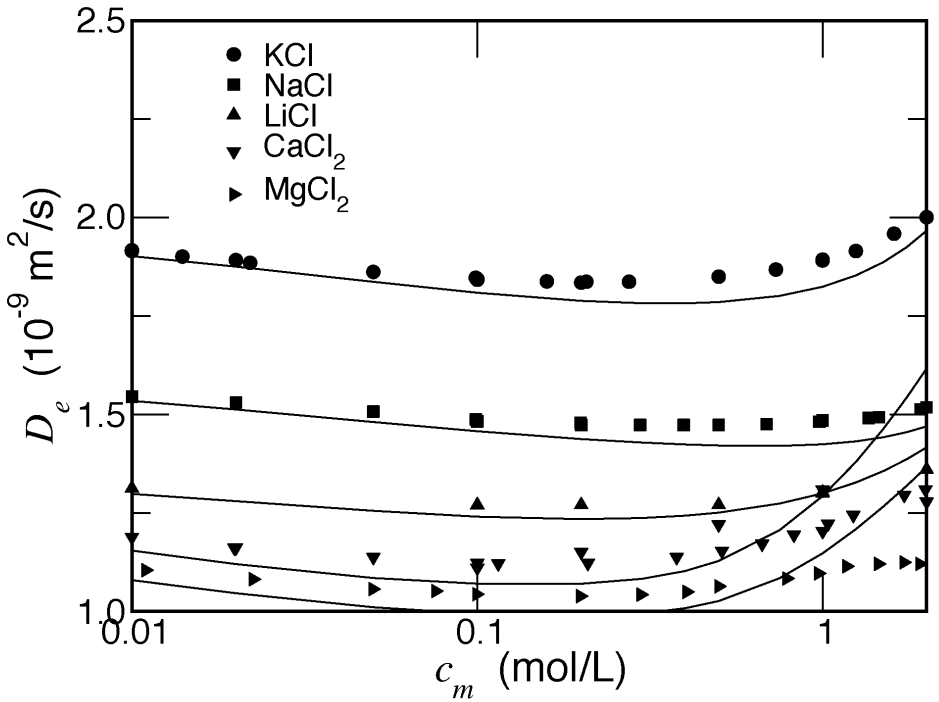


Binary Diffusion

$$D_i = D_i^s$$

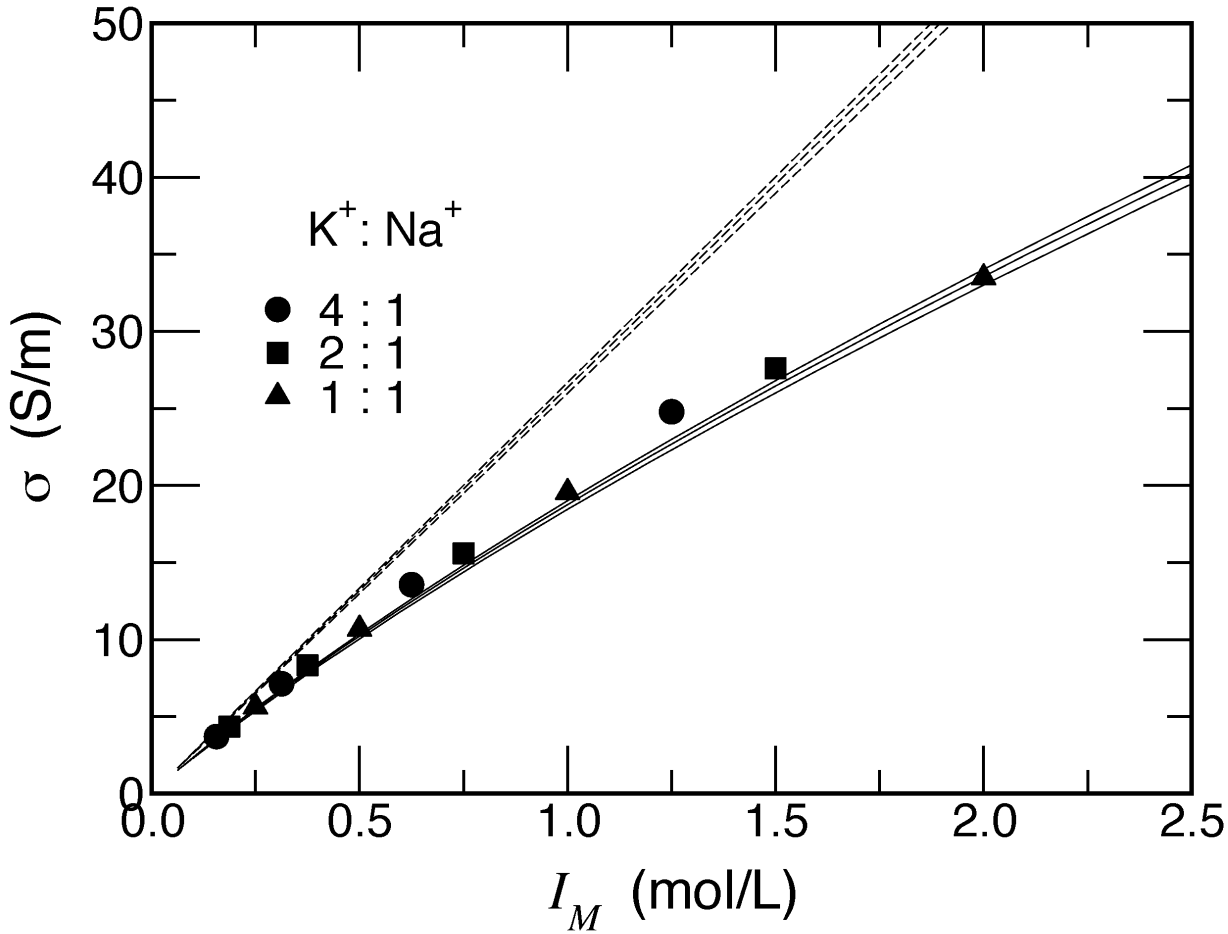
$$D_i = D_i^s \left(\frac{\eta_w}{\eta_{soln}} \right)$$





Solution Conductivity

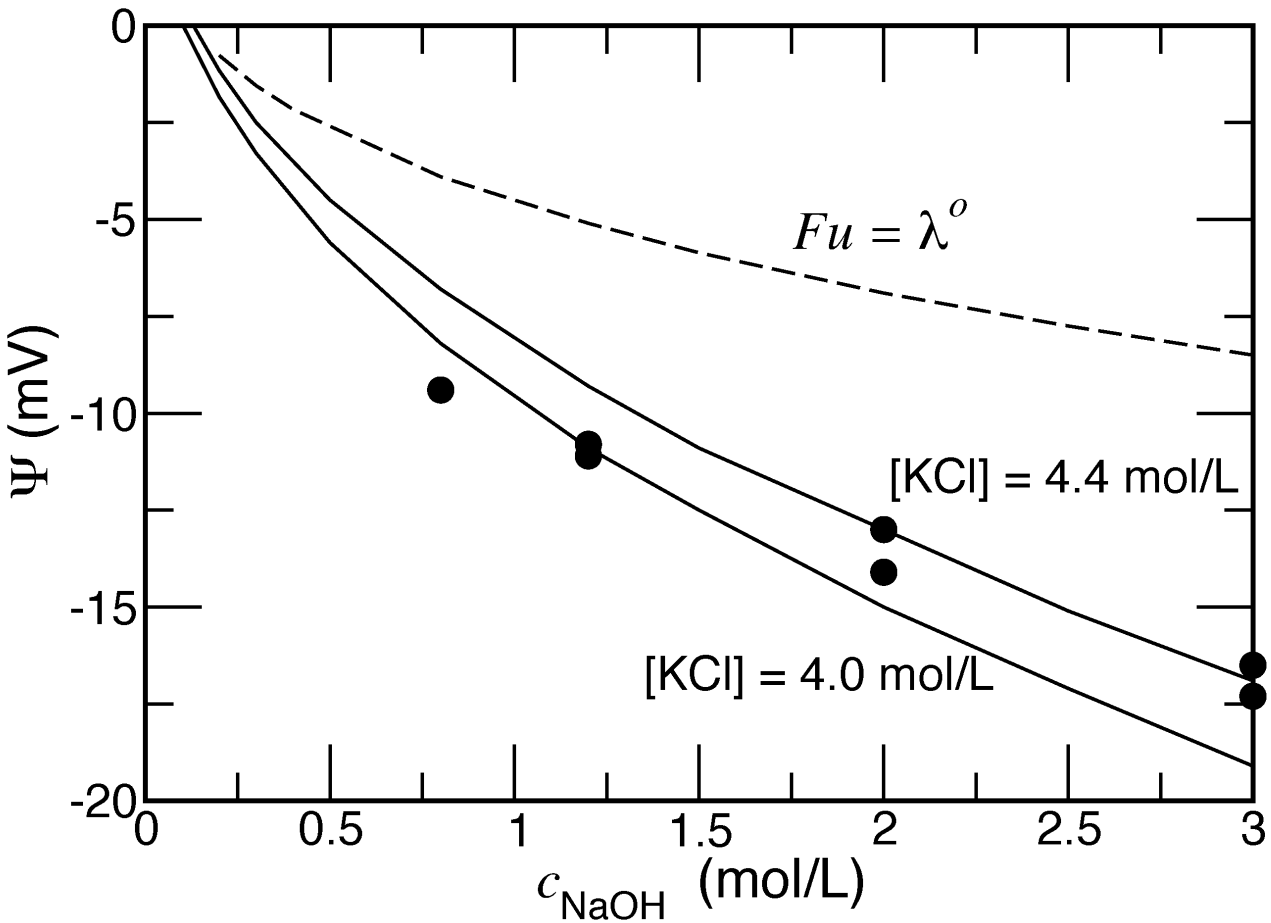
KOH + NaOH



Snyder, Feng, Keen, and Mason, *Cem. Concr.Res.*, **33**, 793-798, 2002.

Liquid Junction Potential

KCl(sat) || NaOH

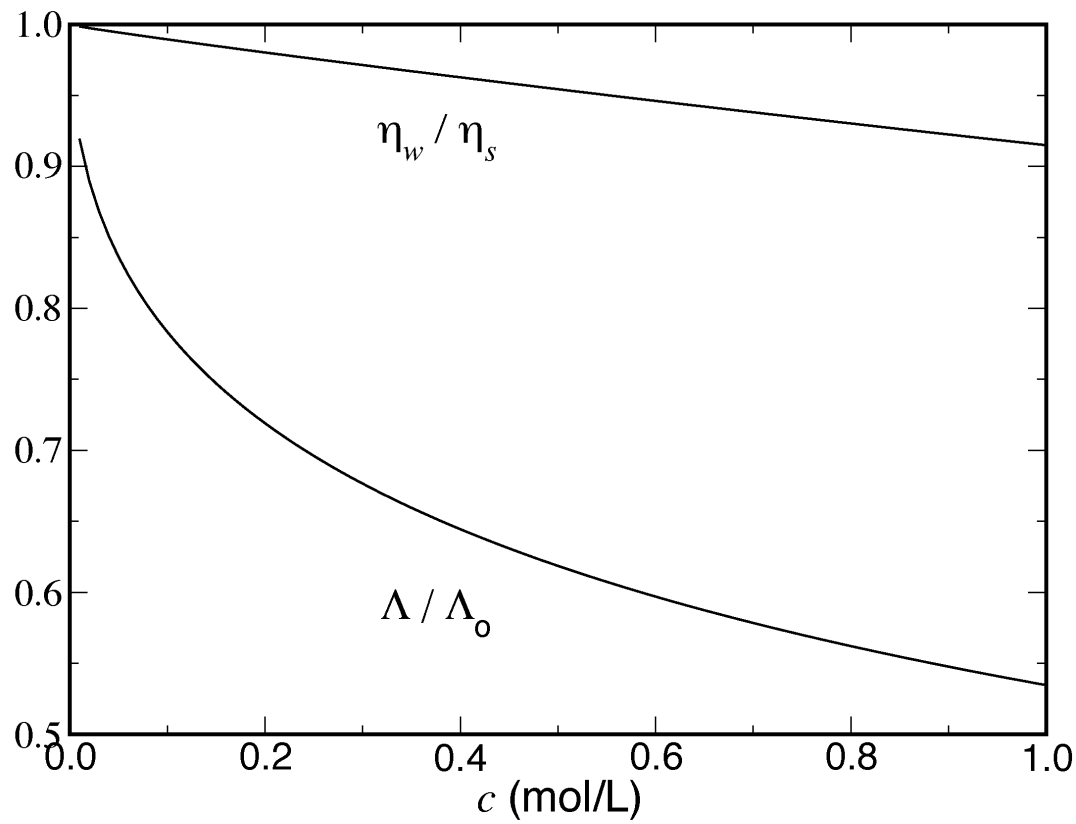


Norkus and Vaskelis, *Electroanalysis*, **8**, 171-172, 1996.

D(c) vs. u(c)

$$\frac{\eta_{\mathrm{w}}}{\eta_{\mathrm{soln}}} \quad \text{vs.} \quad \sum_i \frac{1}{1 + G_i I_M^{1/2}}$$

NaCl



Bulk Transport

Pore Space:

$$\mathbf{j}_i^p = \tau^{-1}\,\mathbf{j}_i$$

Bulk Porous Material:

$$\mathbf{j}_i^b = \frac{\theta}{\tau}\,\mathbf{j}_i$$

Bulk Transport:

$$\mathbf{j}_i^b = -\frac{LD_i}{RT}\,c_i\nabla\mu_i - z_i L u_i c_i \nabla\psi \qquad L = \frac{\theta}{\tau}$$

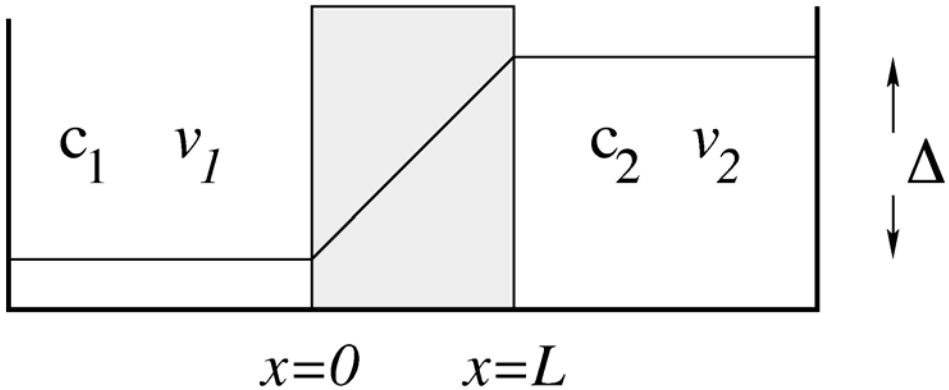
Laboratory Validation

- Alumina frit: 500 nm pores
- Temperature control: 25 ^{o}C
- Potassium Iodide: I^-
- Counter-diffusing binary salt
- Constant water activity
- Formation Factor: $L = \sigma_{\text{bulk}} / \sigma_{\text{soln}}$

Laboratory Validation

Assumption: Fick's Law

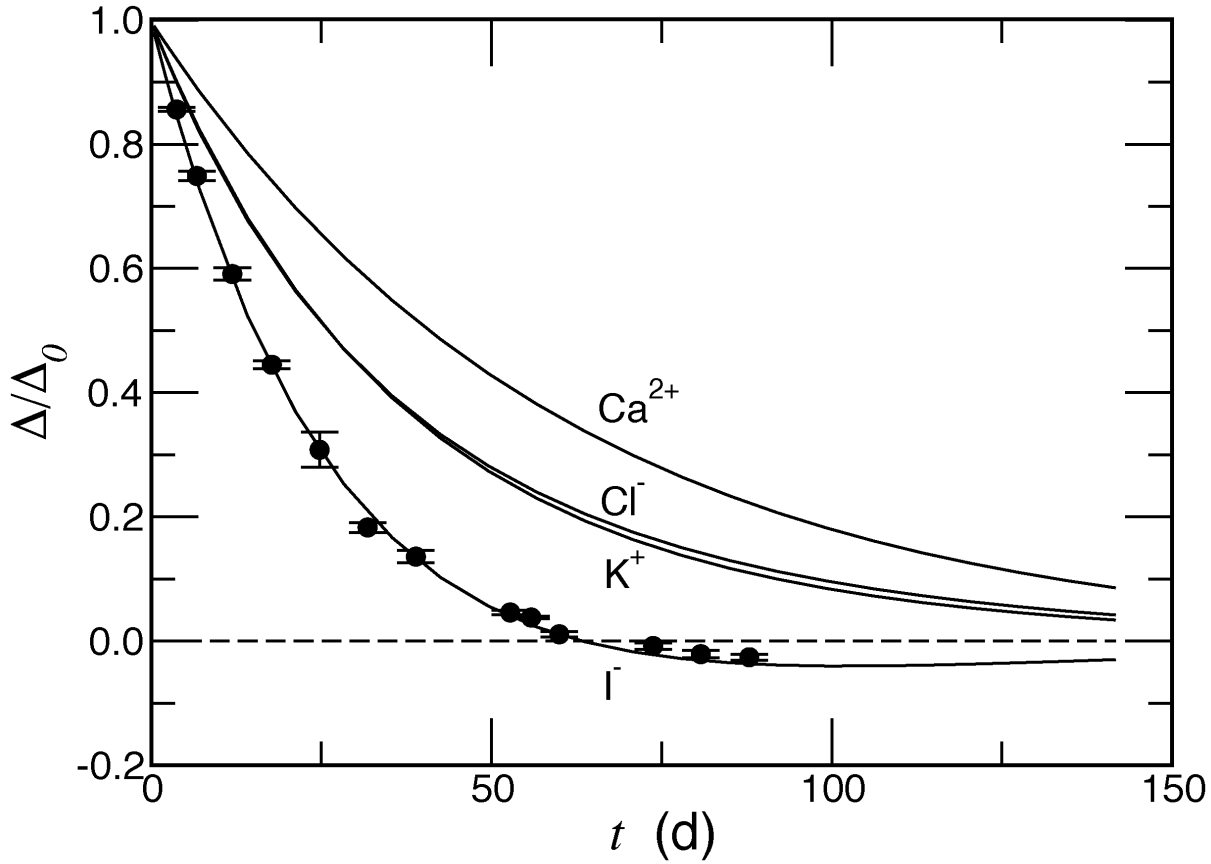
- Flux is constant
- $\Delta_\circ = (c_2 - c_1)$ at $t = 0$
- $\Delta = c_2 - c_1$



$$\frac{\Delta}{\Delta_\circ} = \exp\left[\frac{-AD^*}{L}\left(\frac{1}{v_1} + \frac{1}{v_2}\right)t\right]$$

Laboratory Validation

KI - $CaCl_2$



Snyder and Marchand, *Cem. Concr.Res.*, **31**, 1837-1845, 2001.

Bulk Migration: Applied Voltage

Macroscopic Electroneutrality: $l \gg \kappa^{-1}$

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \mathbf{J} = 0$$

$$\nabla \cdot \mathbf{J} = 0$$

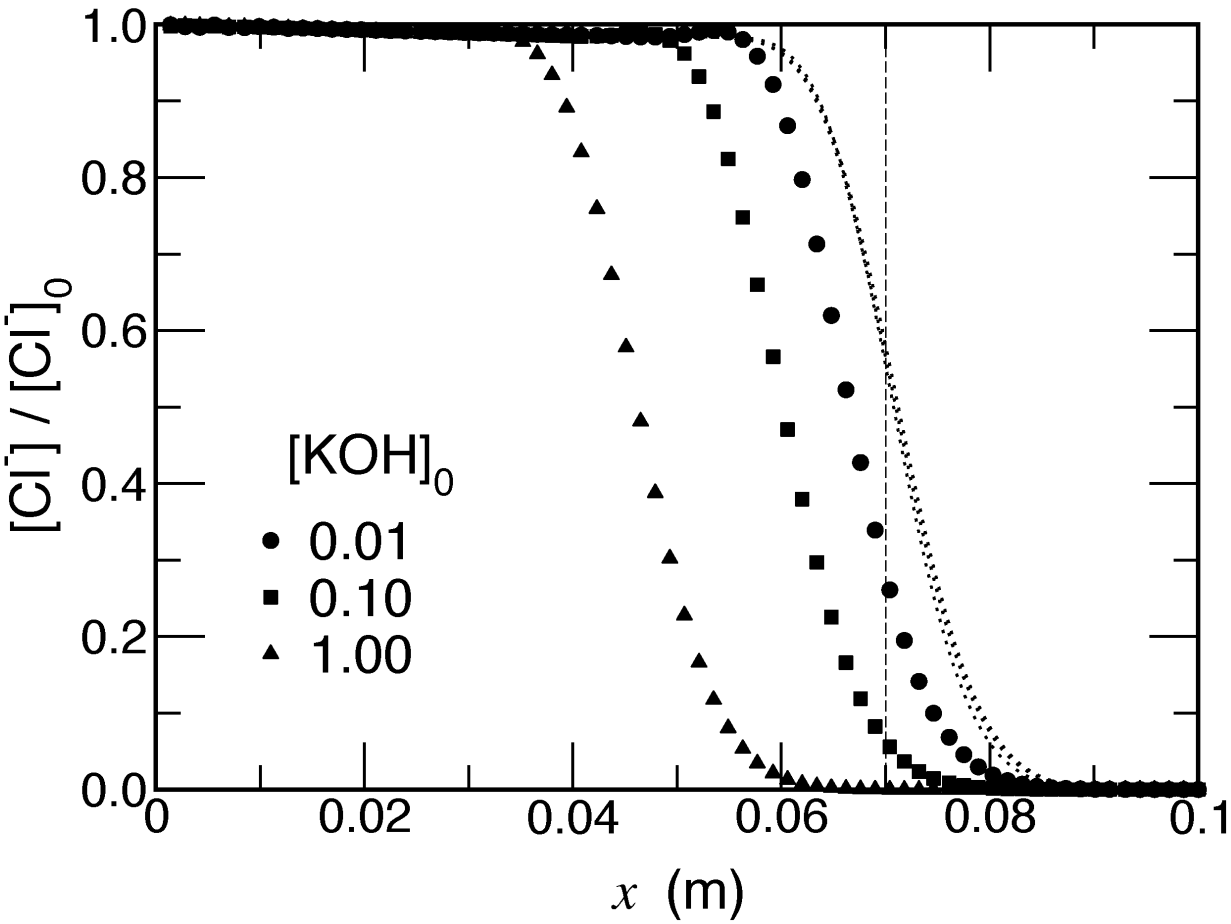
$$\Delta V_n = \widetilde{V} \frac{1/\sigma_n}{\sum_n 1/\sigma_n}$$

$$\widetilde{V} = V_{ext} - V_{DP}$$

Bulk Migration: Applied Voltage

L = 0.10 m A = 0.001 m2 ψ_{ext}=10 V

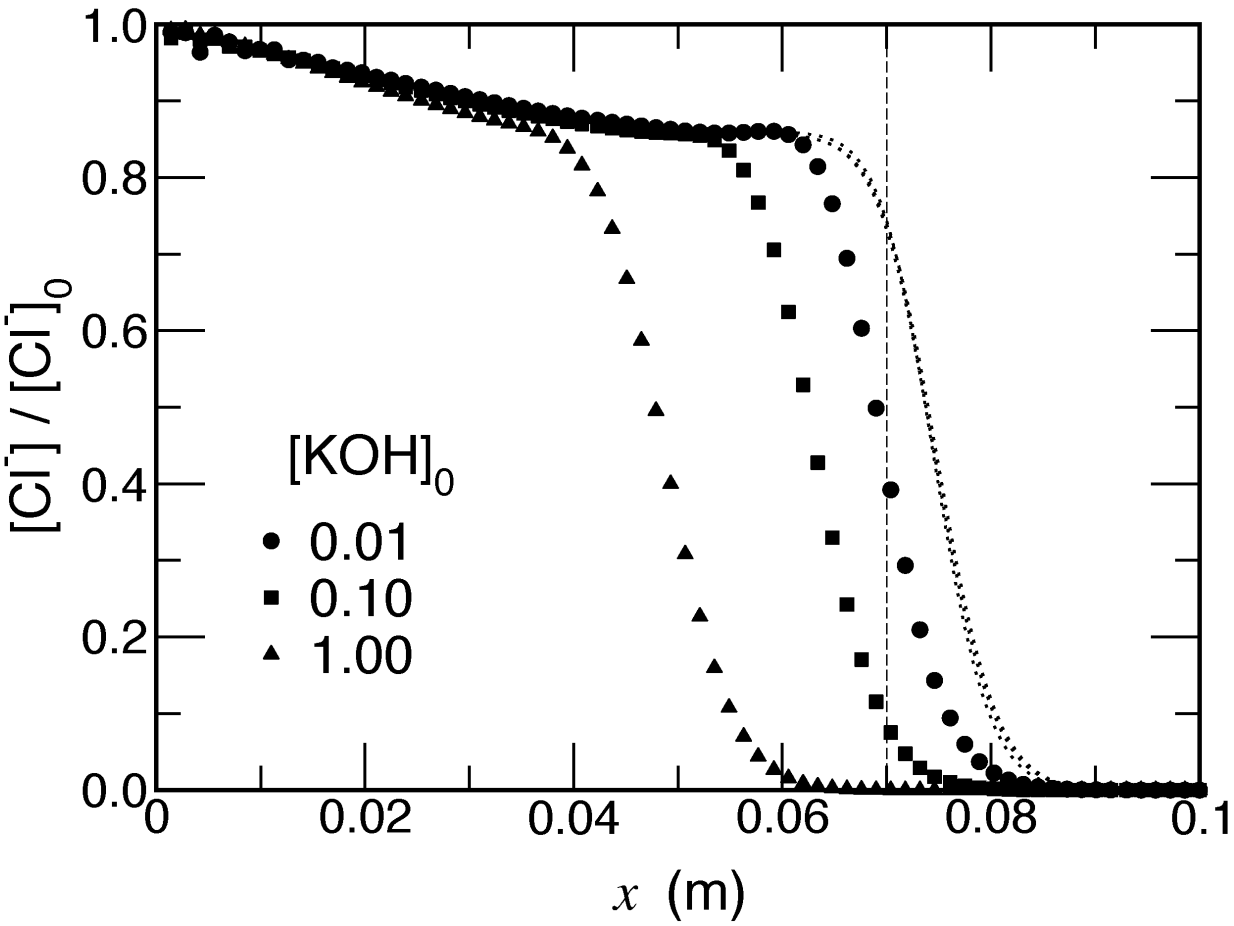
$$\frac{[\text{NaCl}]}{[\text{KOH}]} = 0.01$$



Bulk Migration: Applied Voltage

L = 0.10 m A = 0.001 m2 ψ_{ext}=10 V

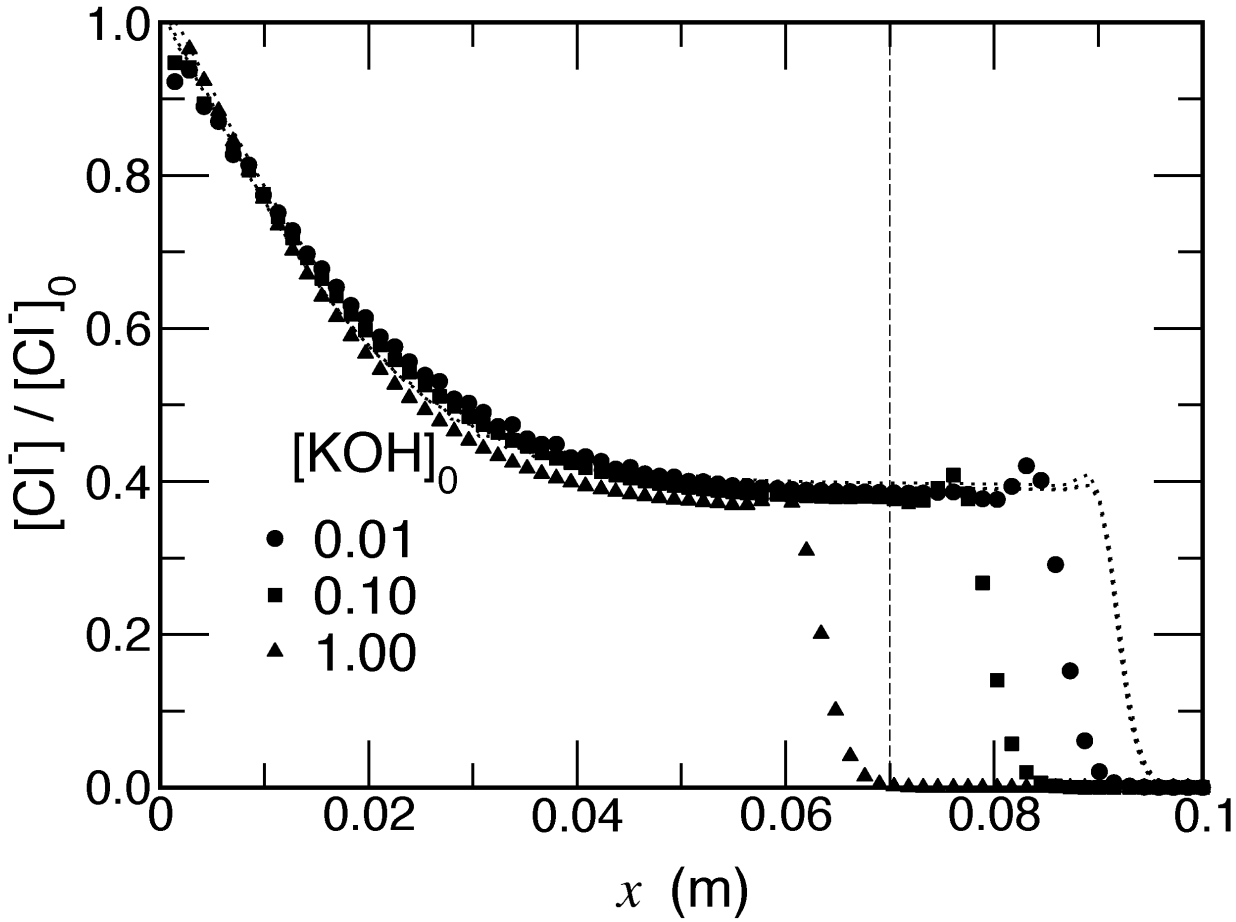
$$\frac{[\text{NaCl}]}{[\text{KOH}]} = 0.10$$



Bulk Migration: Applied Voltage

L = 0.10 m A = 0.001 m2 ψ_{ext}=10 V

$$\frac{[\text{NaCl}]}{[\text{KOH}]} = 1.00$$



Future Work

- Redox reactions and kinetics
- Osmotic effects
- Moisture transport
- Temperature dependence
- Binding