

Can Resistivity/Conductivity Measurements Really Capture Long-Term Chloride Resistance?

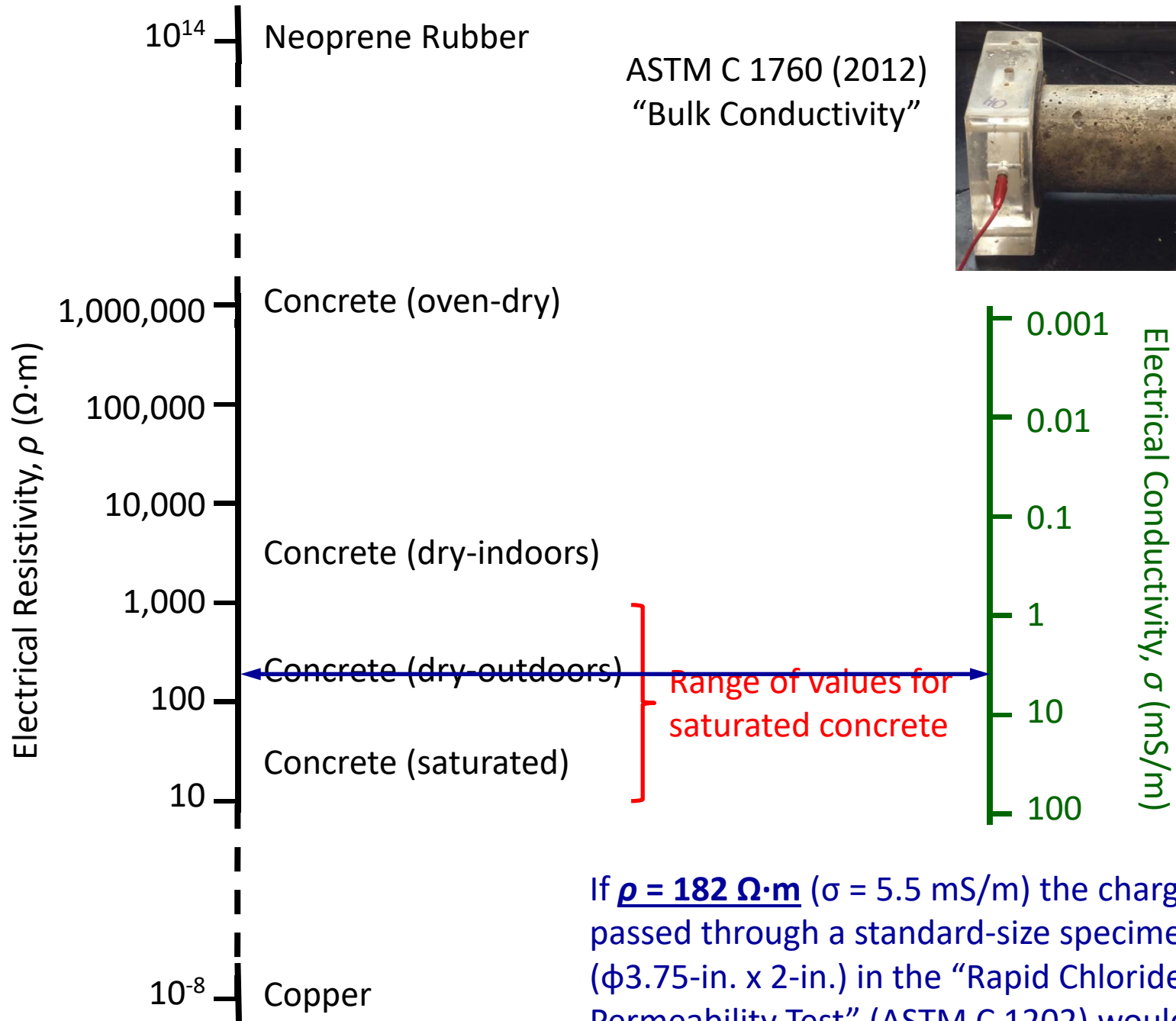


Michael Thomas

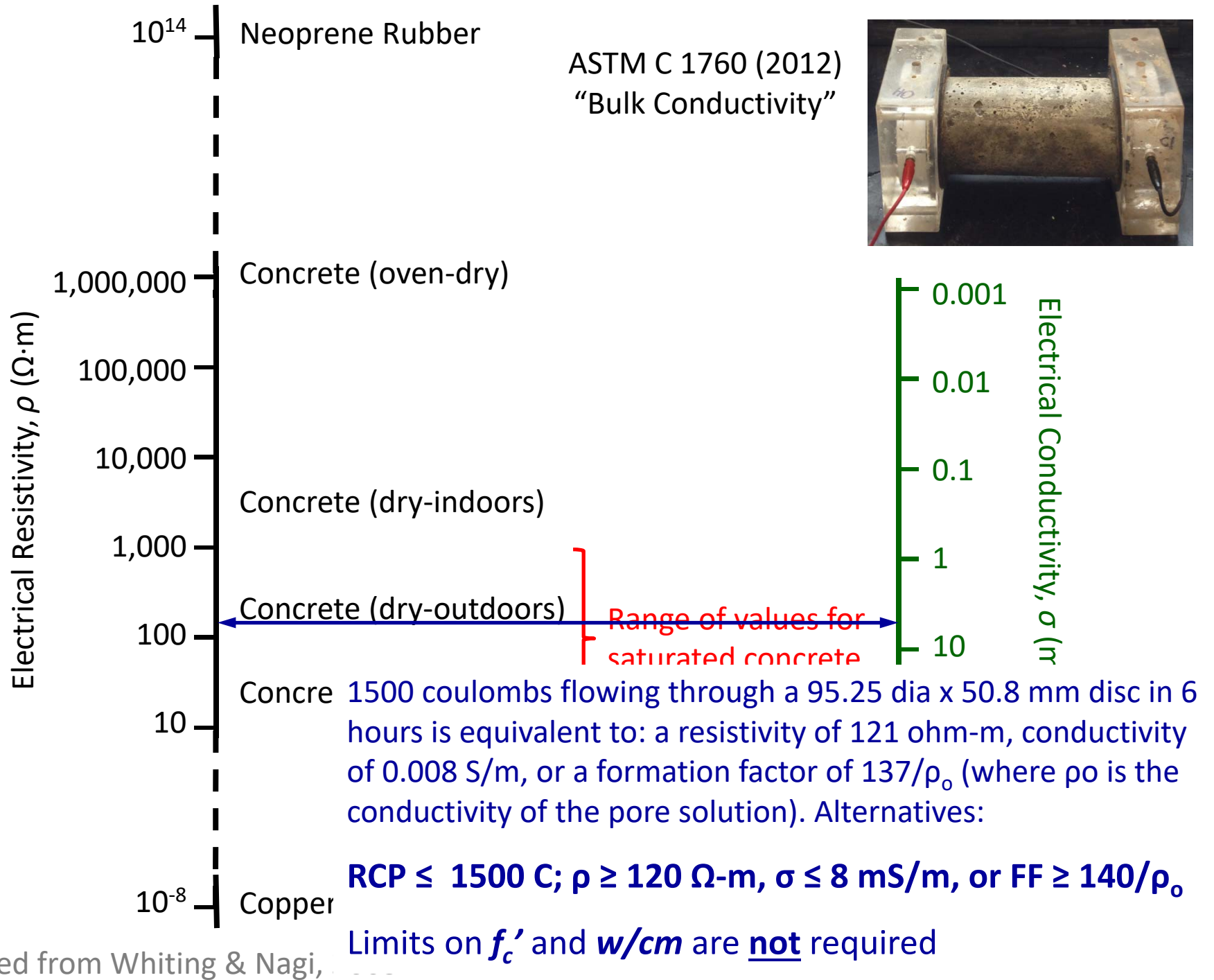
University of New Brunswick

Chloride Specifications in Concrete Construction: Part 1 Issues & Ideas

Anna Maria Workshop XVIII: Chemical Attack on Concrete, November 2017

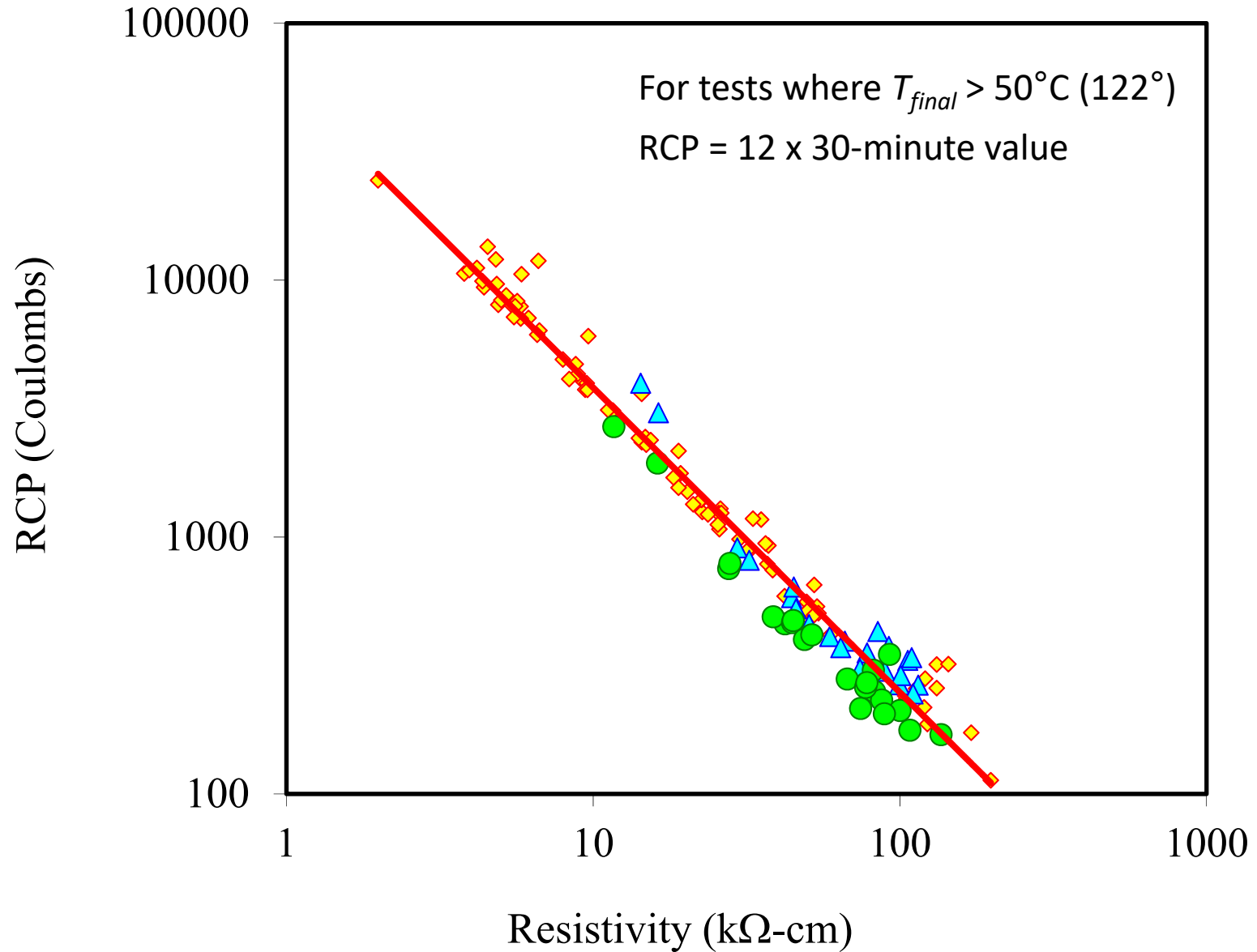


If $\rho = 182 \Omega \cdot m$ ($\sigma = 5.5 \text{ mS/m}$) the charge passed through a standard-size specimen ($\phi 3.75\text{-in.} \times 2\text{-in.}$) in the "Rapid Chloride Permeability Test" (ASTM C 1202) would be approximately **1000 Coulombs** (6h at 60V)

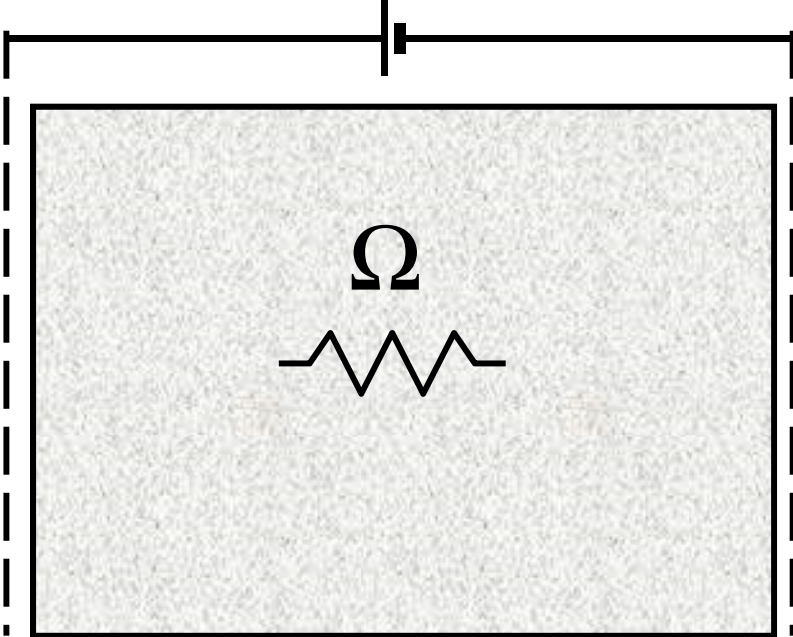


Adapted from Whiting & Nagi,

RCPT vs. Electrical Resistivity

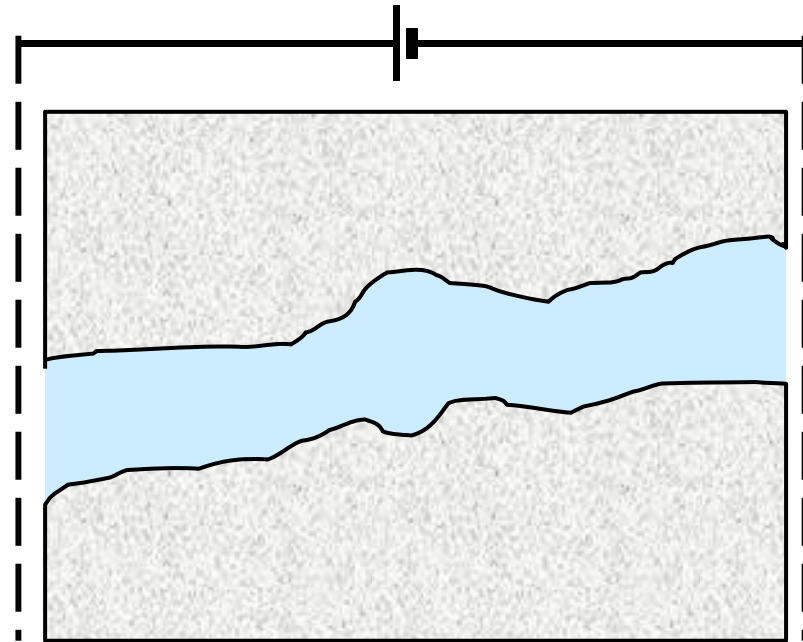


Electrical resistance of saturated concrete is primarily dependent on:



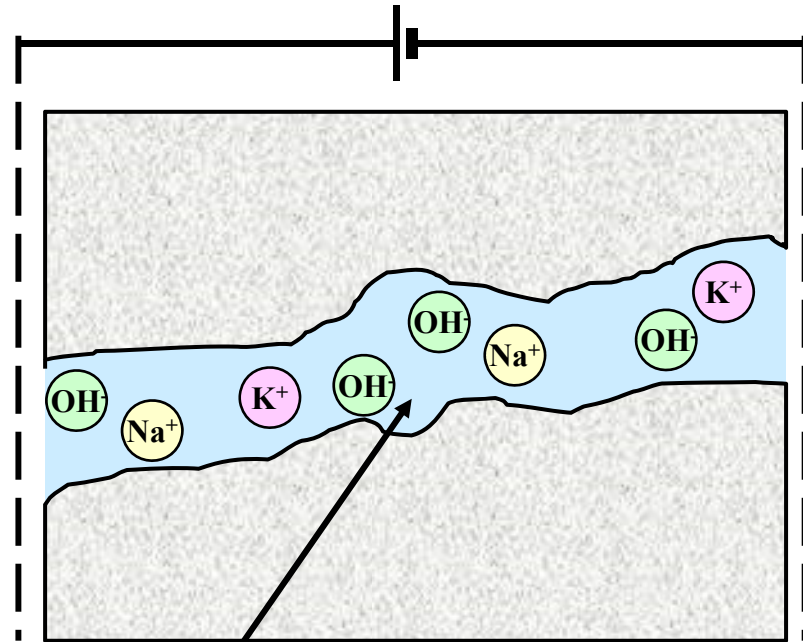
Electrical resistance of saturated concrete is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores



Electrical resistance of saturated concrete is primarily dependent on:

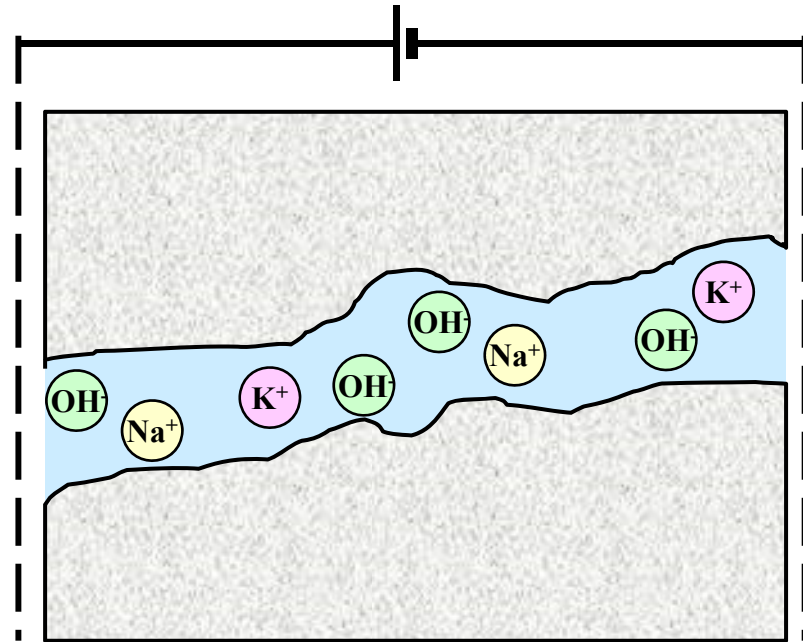
- Pore structure
 - Volume, size & connectivity of pores
- Composition of pore solution
 - Concentration of ions



More ions in solution – increased electrical conductivity – i.e. reduced electrical resistance

Electrical resistance of saturated concrete is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores
- Composition of pore solution
 - Concentration of ions

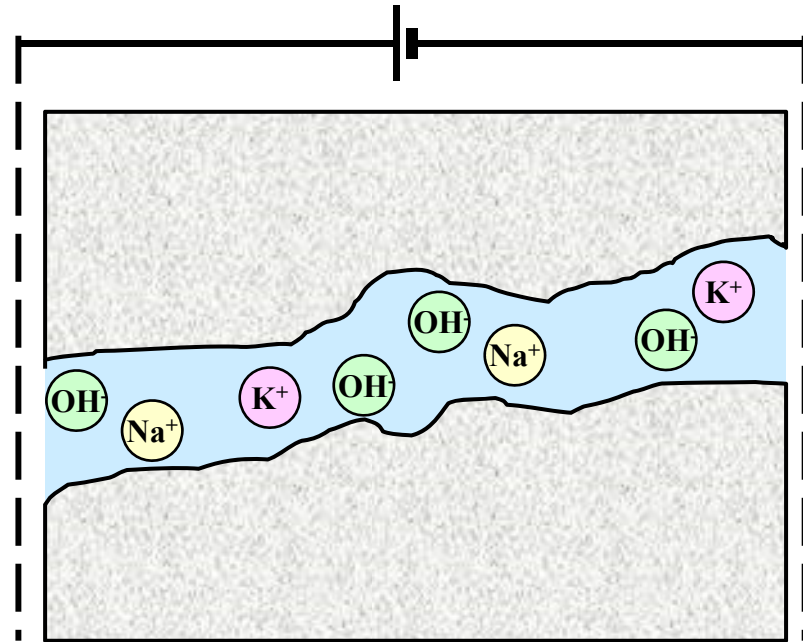


Chloride resistance of saturated concrete is primarily dependent on:



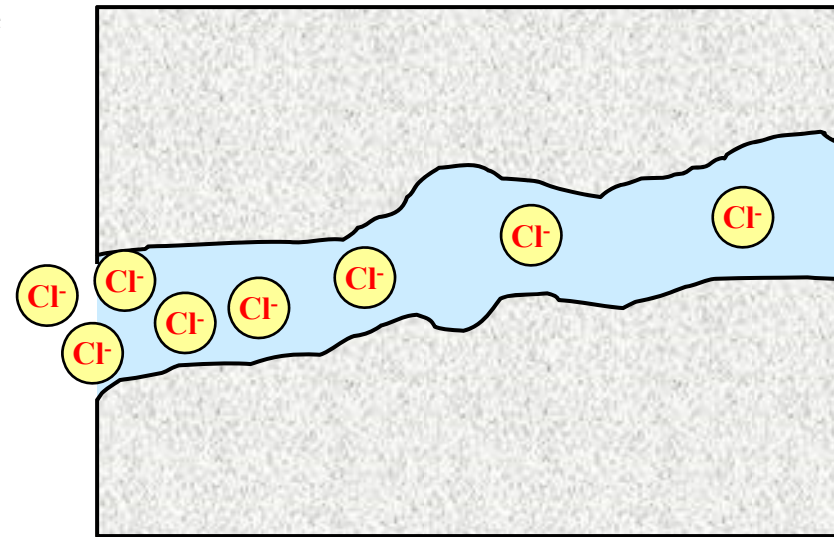
Electrical resistance of saturated concrete is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores
- Composition of pore solution
 - Concentration of ions



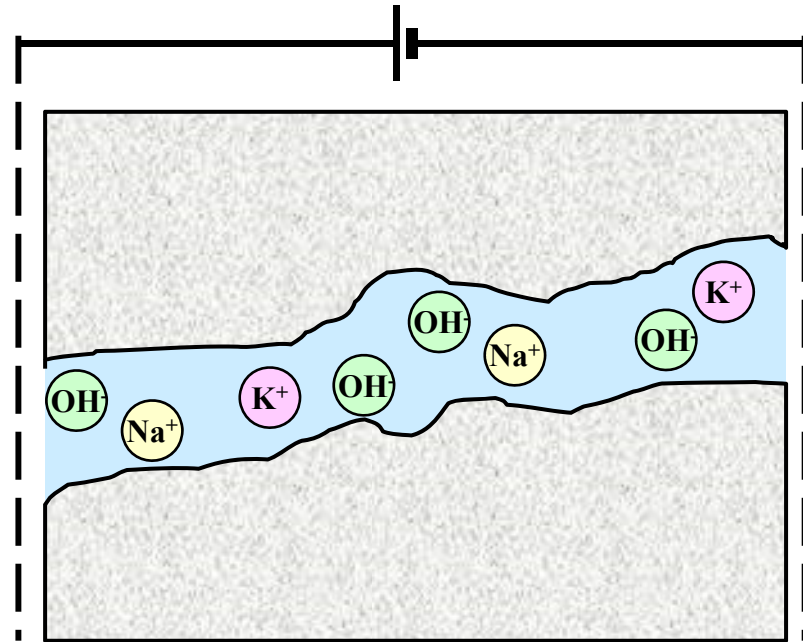
Chloride resistance of saturated concrete is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores



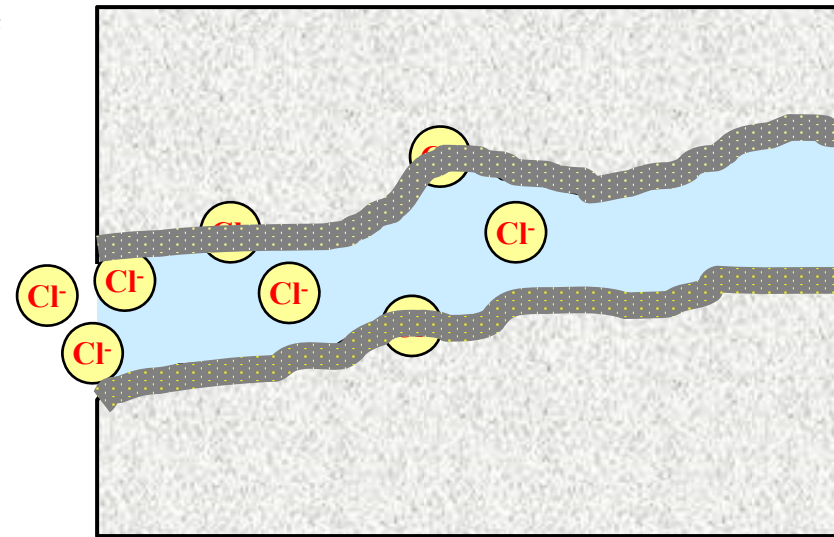
Electrical resistance of saturated concrete is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores
- Composition of **pore solution**
 - Concentration of ions



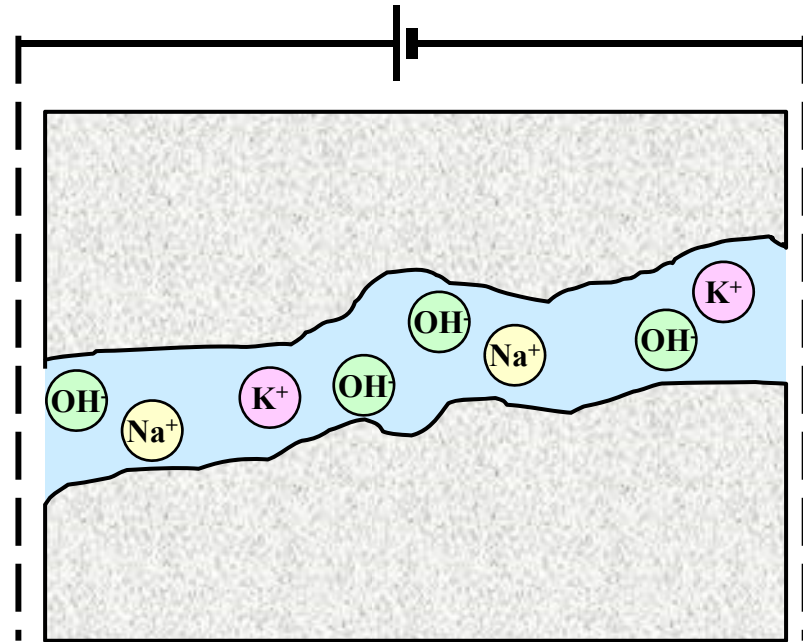
Chloride resistance of saturated concrete is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores
- Composition of **cement hydrates**
 - Ability of hydrates to bind chlorides



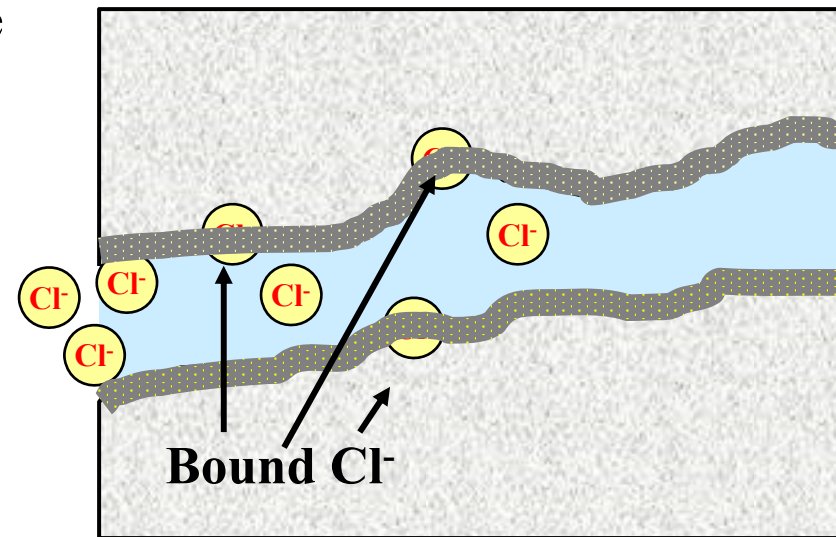
Electrical resistance of saturated concrete is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores
- Composition of pore solution
 - Concentration of ions



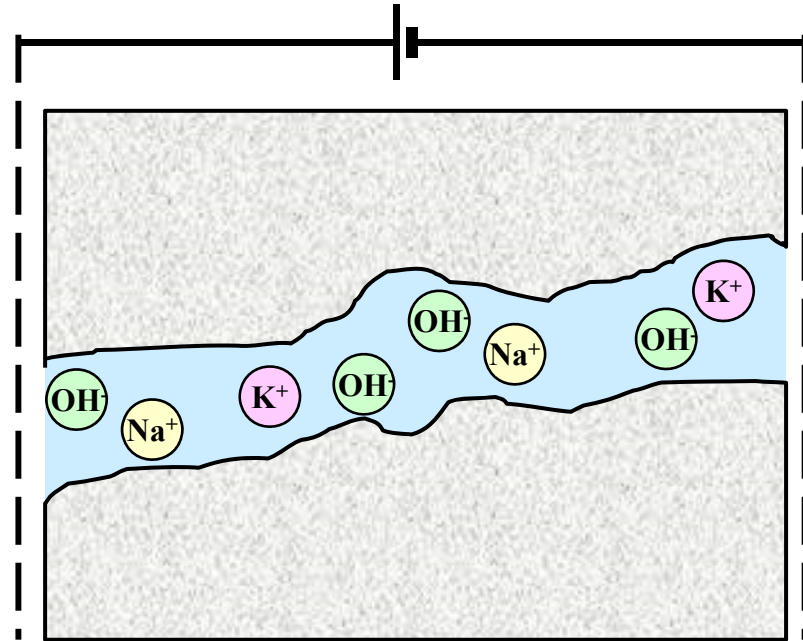
Chloride resistance of saturated concrete is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores
- Composition of cement hydrates
 - Ability of hydrates to bind chlorides



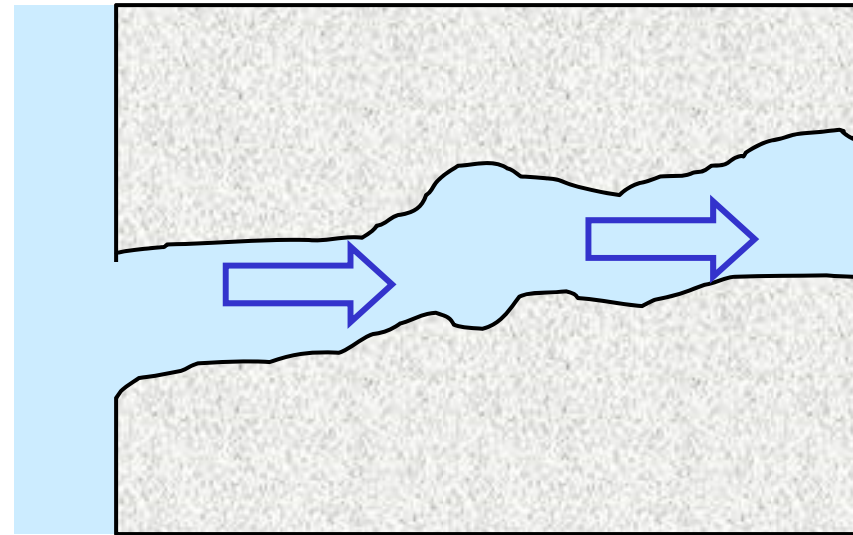
Electrical resistance of saturated concrete is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores
- Composition of pore solution
 - Concentration of ions



Hydraulic conductivity is primarily dependent on:

- Pore structure
 - Volume, size & connectivity of pores



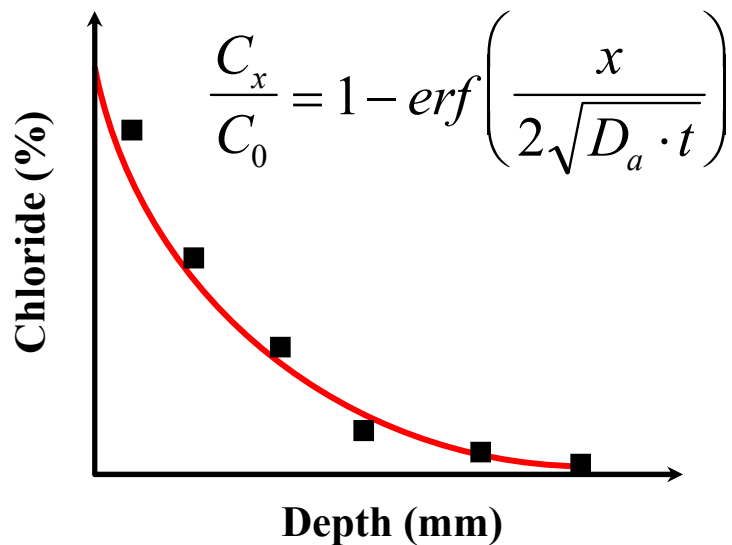
ASTM C 1556 Test to Determine the Bulk Diffusion Coefficient of Concrete

Concrete sample is immersed in NaCl solution for time t (minimum 35 days)

Sample then ground in approx. 1-mm depth increments

Dust samples analyzed for chlorides →

To produce chloride profile ↓

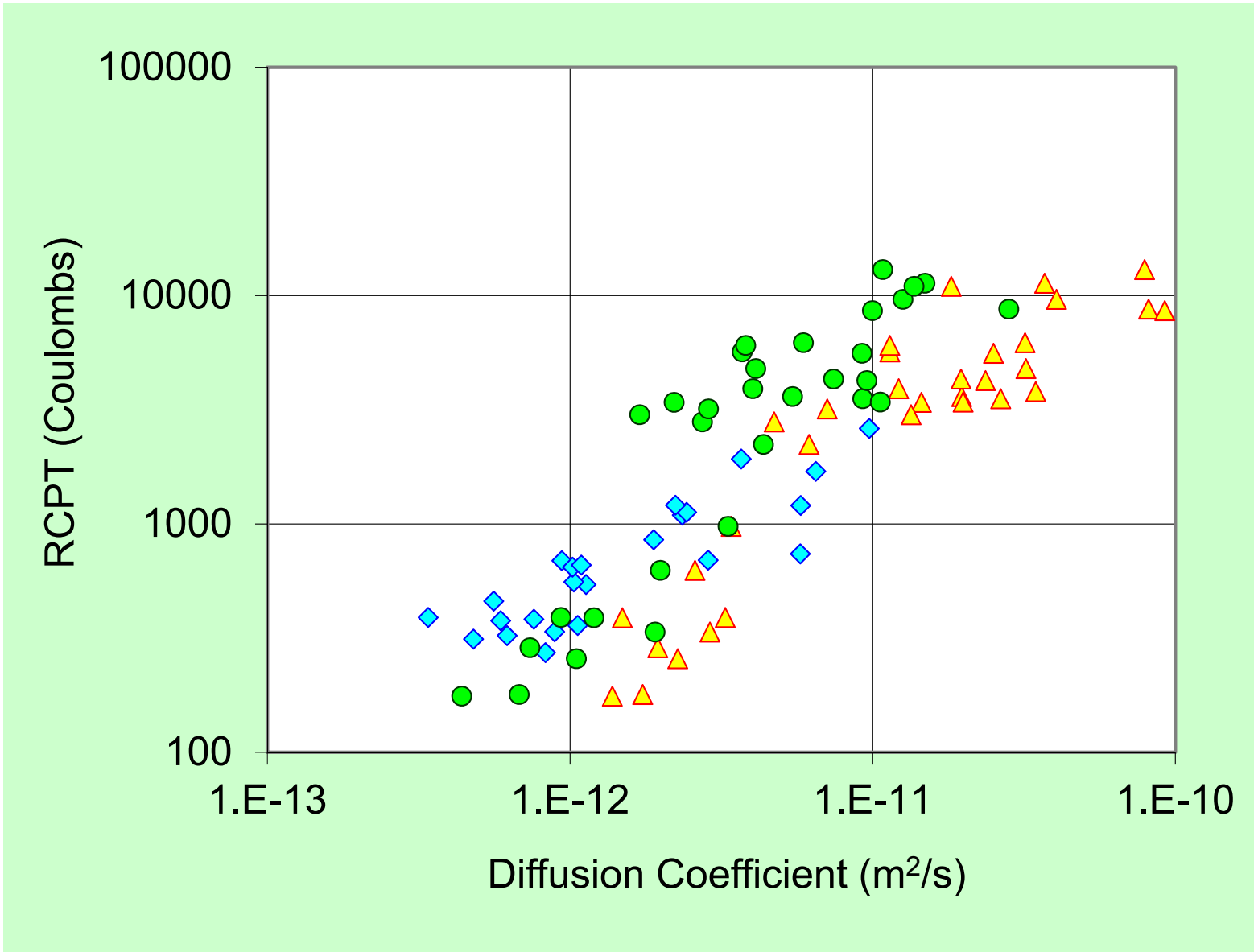


C_0 and D_a found by fitting the equation shown to the measured profile.

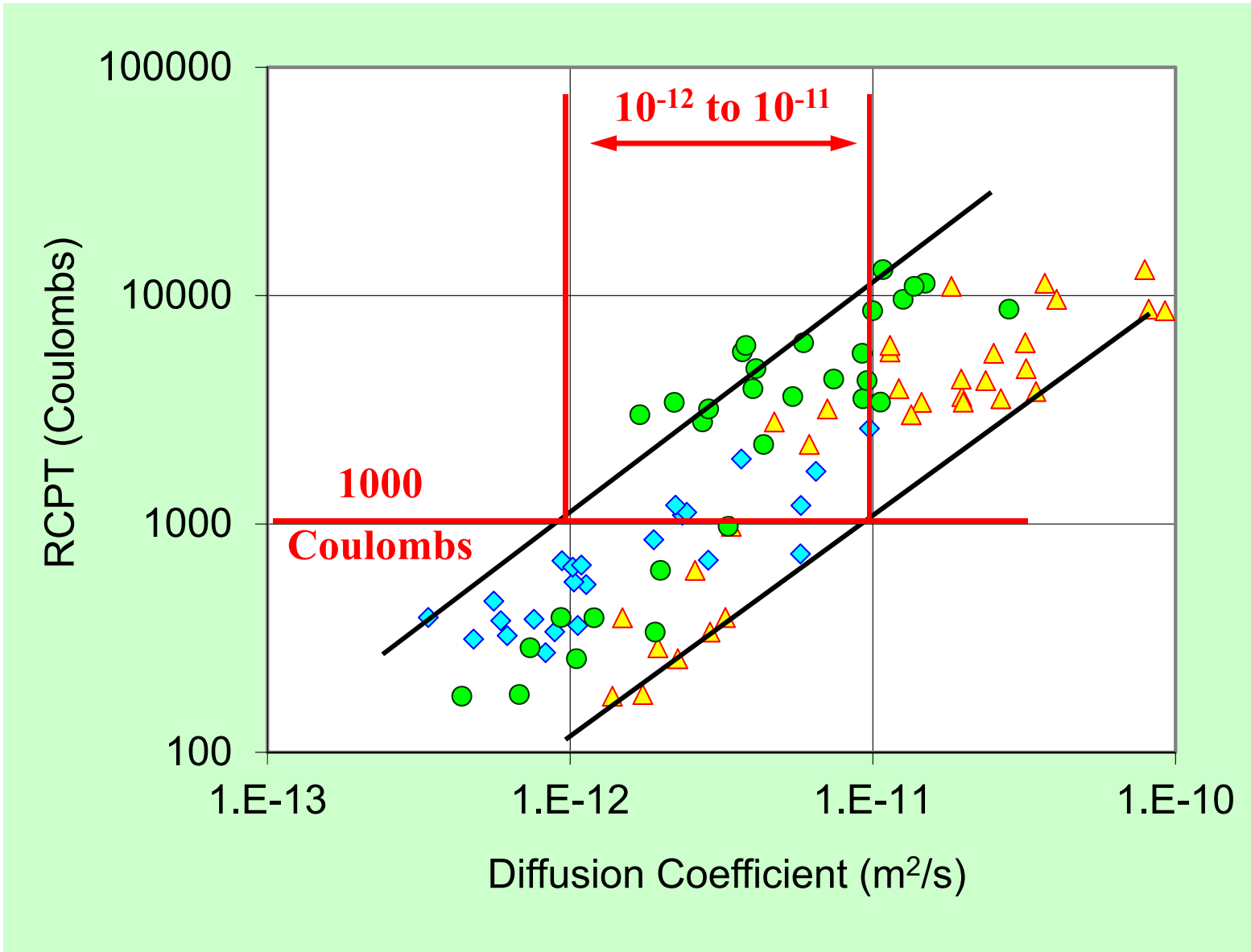
Values of D_a typically in the range:

1×10^{-13} to 1×10^{-11} m²/s

RCPT vs. Bulk Diffusion

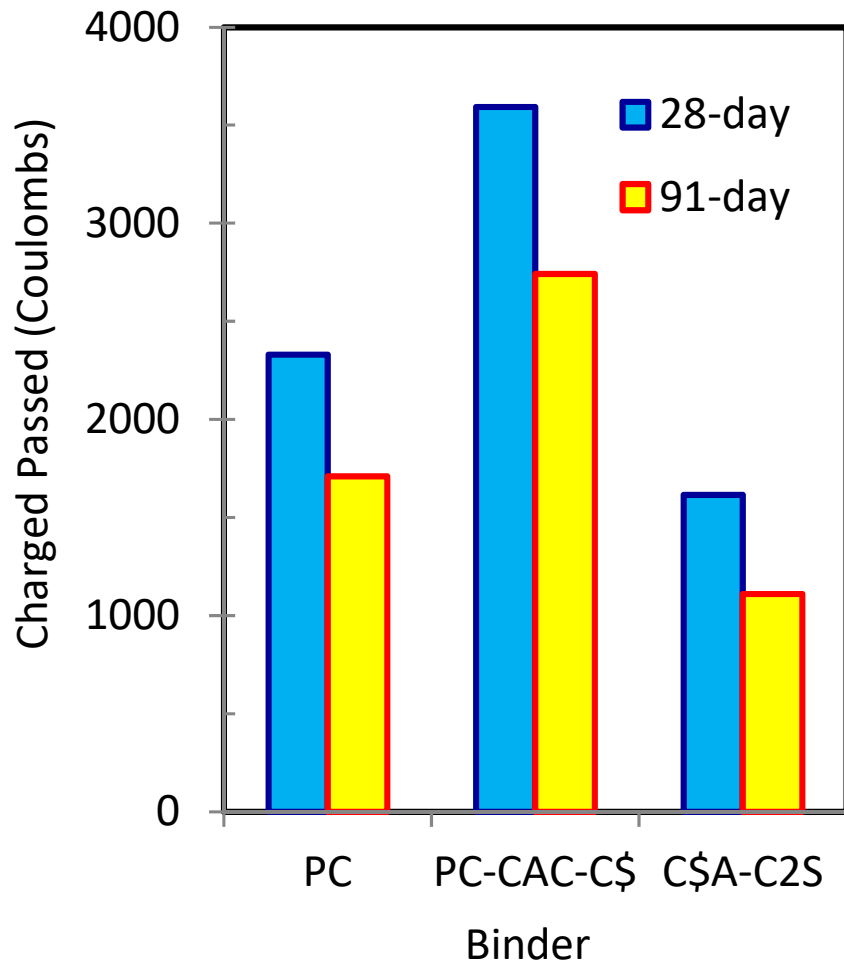


RCPT vs. Bulk Diffusion



Chloride Resistance: Rapid-Set Cements

ASTM C 1202 “Rapid Chloride Permeability”



PC-CAC-C\$ is a ternary blend of:

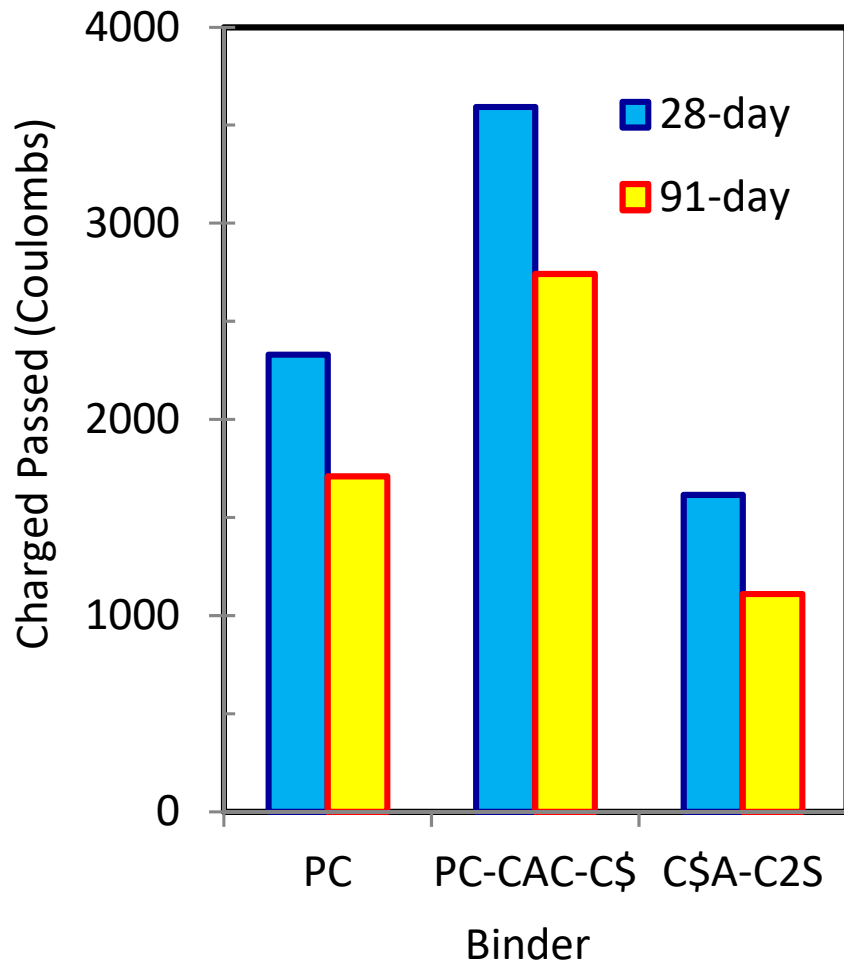
- Portland cement
- Calcium-aluminate cement
- Gypsum

CSA-C2S is a blend of:

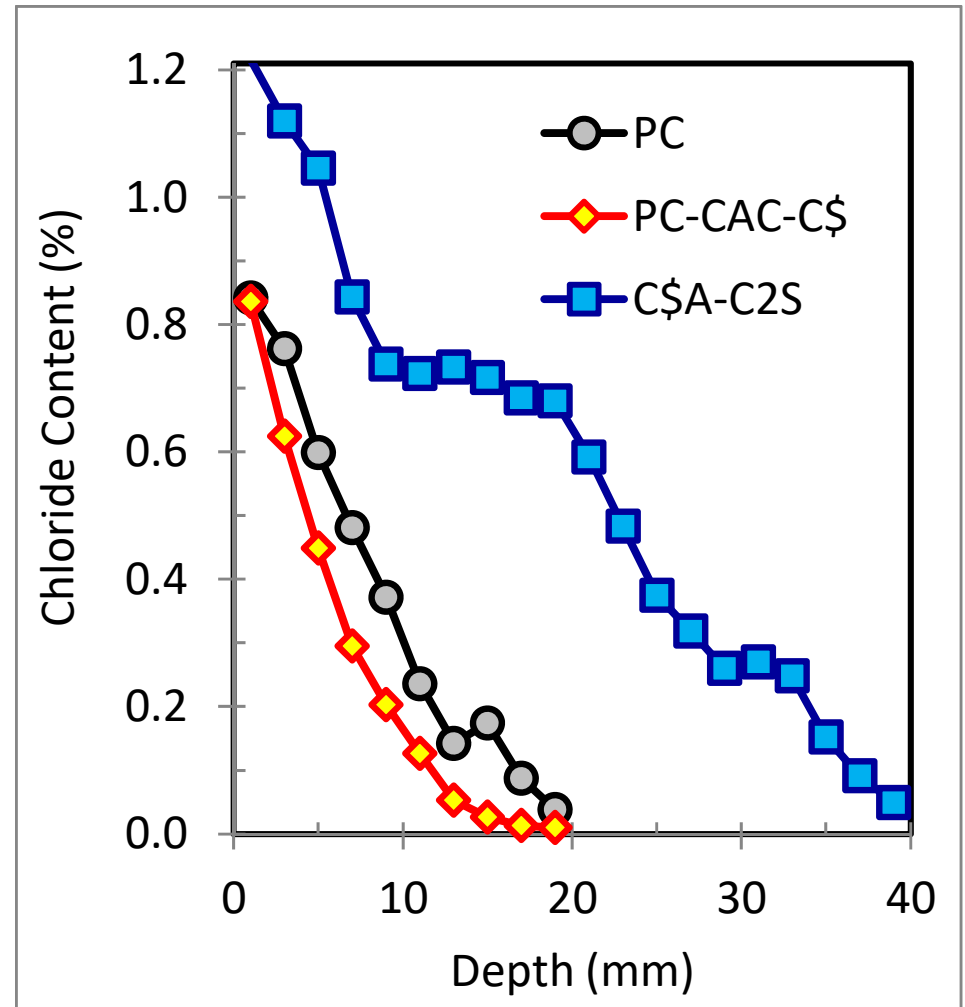
- Calcium-alumino-sulfate (Klein's compound)
- Belite

Chloride Resistance: Rapid-Set Cements

ASTM C 1202 “Rapid Chloride Permeability”

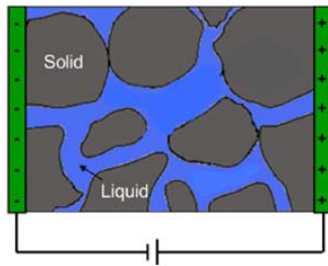


ASTM C 1567 “Chloride Diffusion”



Formation Factor

Formation Factor is a fundamental material property



$$F = \frac{\rho}{\rho_0} = \frac{\text{[Diagram of porous material with battery]}{\text{[Diagram of solid material with battery]}}$$

$$F = \frac{1}{\phi\beta}$$

$$F = \frac{\rho}{\rho_0} = \frac{D}{D_i}$$

F = formation factor

ρ = resistivity of concrete

ρ_0 = resistivity of concrete pore solution

D = chloride diffusion coefficient

D_i = self diffusion coefficient for ion (= 2.032×10^{-9} m²/s for Cl^-)

ϕ = Porosity

β = Tortuosity of pore system

Courtesy Jason Weiss

Formation Factor

Resistivity of the pore solution can be

- (i) assumed (e.g. $\rho_0 = 0.1 \text{ } \Omega\text{-m}$ [$\sigma_0 = 10 \text{ S/m}$] for PC mixes),
- (ii) estimated (e.g. “NIST model”) – mill certs and mix proportions
- (iii) measured (by pore-solution extraction)

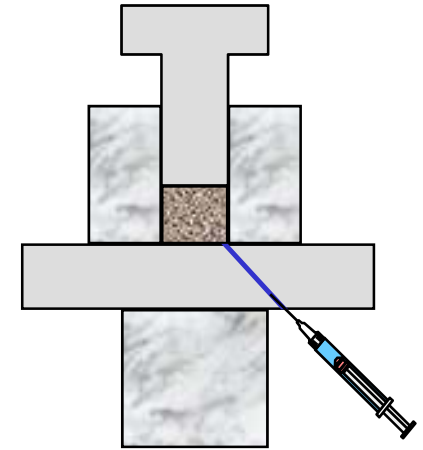
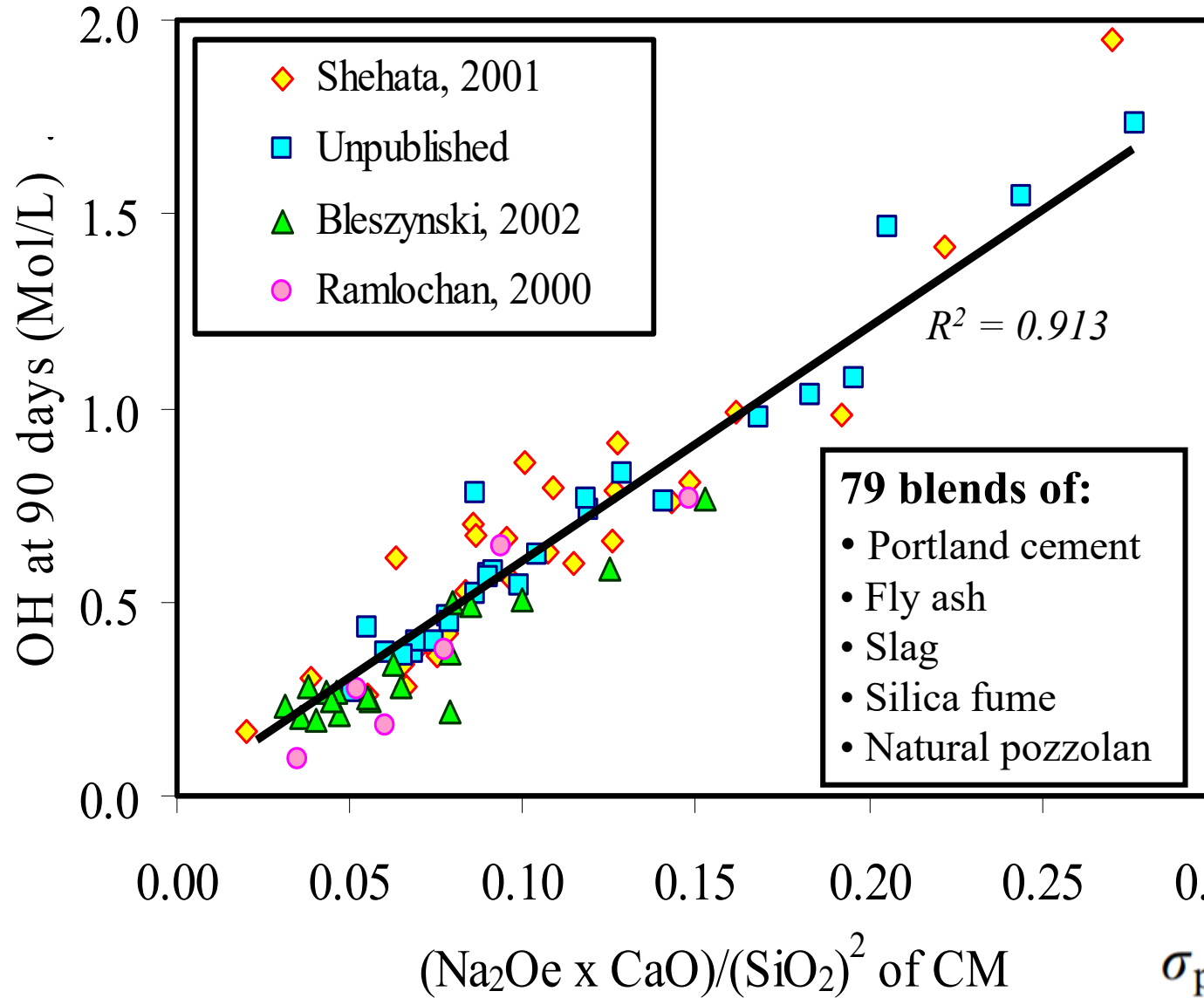
then:

1. F could be used to specify concrete
(correcting resistivity for pore solution effects)
2. F could be used to determine D from measurement of ρ

$$D = D_i \frac{\rho}{\rho_0}$$



Cement Composition & Pore Solution Alkalinity



Results for cement pastes:

w/cm = 0.50

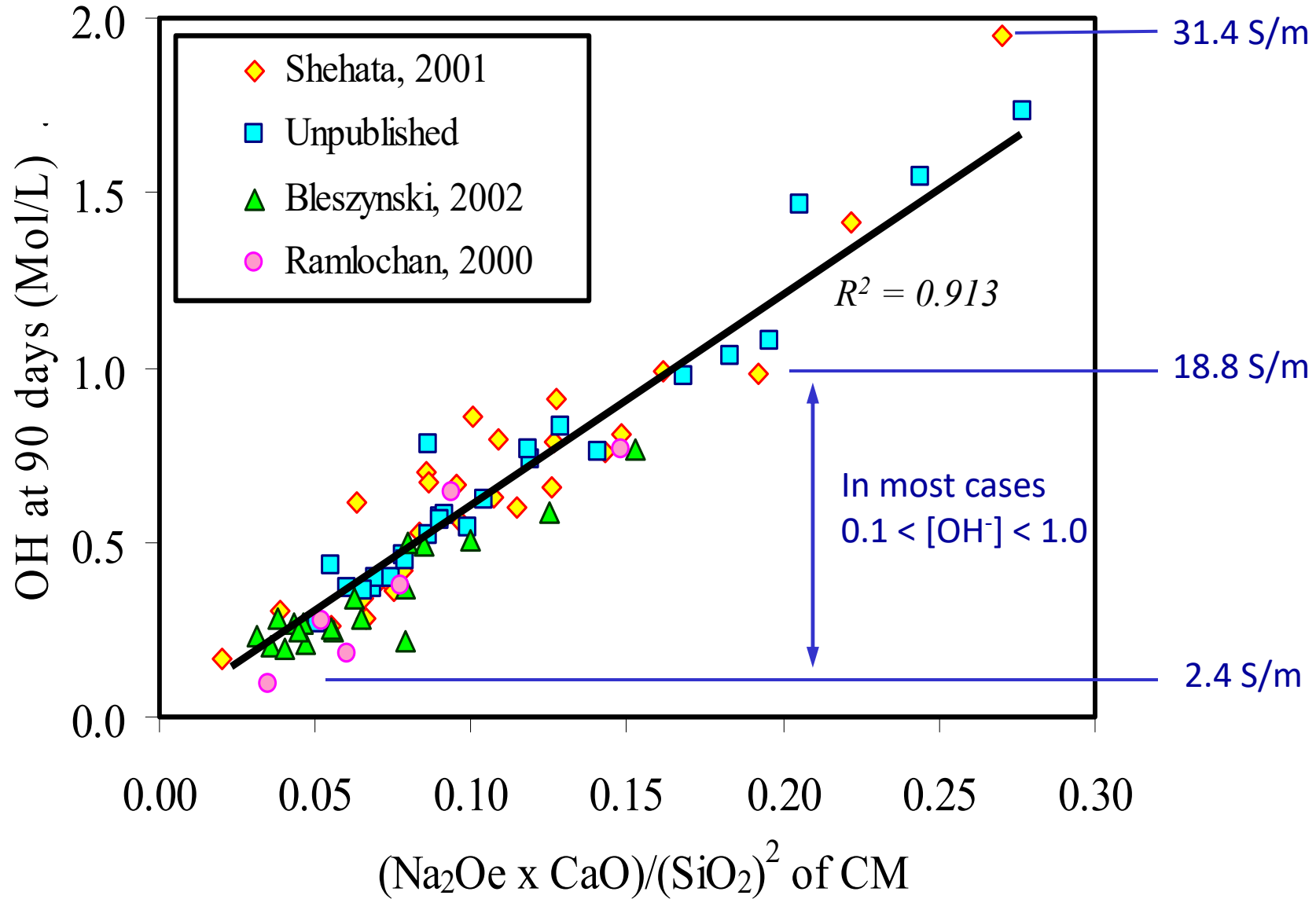
OH⁻ by titration

Na⁺ & K⁺ by flame photometry, atomic absorption or ICP

OH⁻ ~ Na⁺ + K⁺

$$\sigma_{\text{poresoln}} = \sum_i z_i c_i \lambda_i$$

Cement Composition & Pore Solution Alkalinity



Mixture Proportions

Material	Mass (kg or lb)	Na ₂ O content (mass %)	K ₂ O content (mass %)	SiO ₂ content (mass %)
Water	200	Not applicable	Not applicable	Not applicable
Cement	360	0.5	1.3	Not applicable
Silica fume	40	0.2	0.3	99.0
Fly ash	0	8	0.5	50.0
Slag	0.0	0.2	0.5	Not applicable

Estimated system degree of hydration (%):

[Hydrodynamic viscosity of pore solution relative to water:](#)

Curing: Saturated Sealed

Estimated pore solution composition (M):

K+:

Na+:

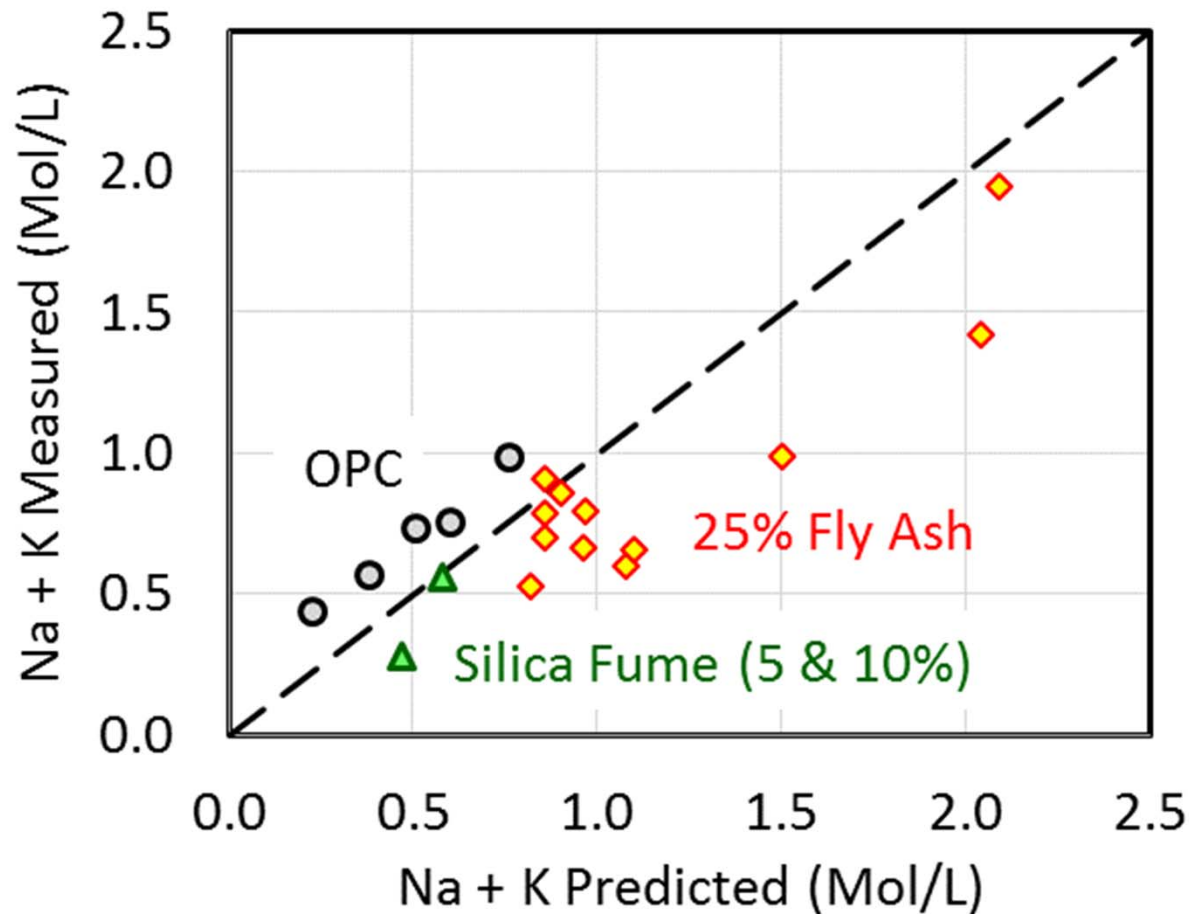
OH-:

Estimated pore solution conductivity (S/m):

Effective water-to-cement ratio: Free alkali ion factor:

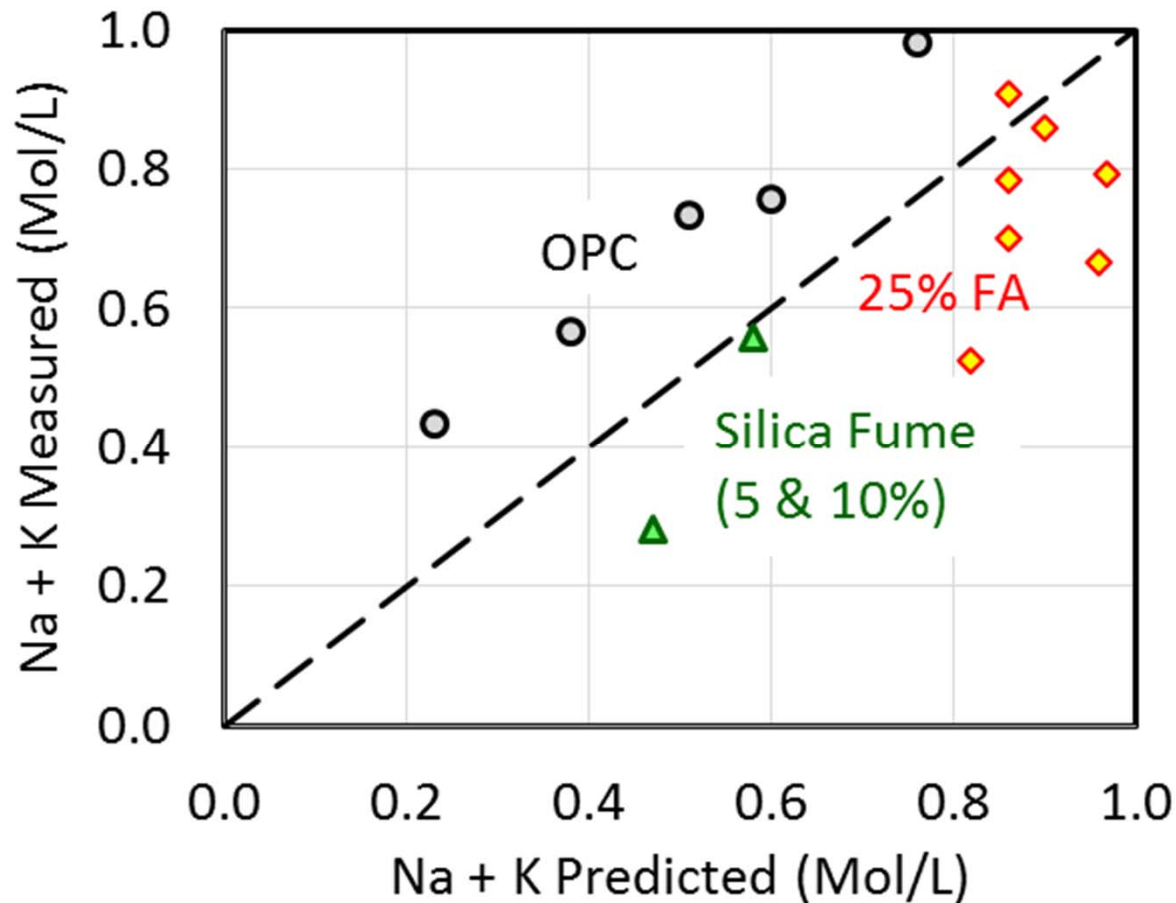
Comparison of Predicted vs Measured Values

- Measurements made on pore solution pressed from hardened paste samples at 90 days
- Predictions made using NIST - <https://ciks.cbt.nist.gov/poresolncalc.html>

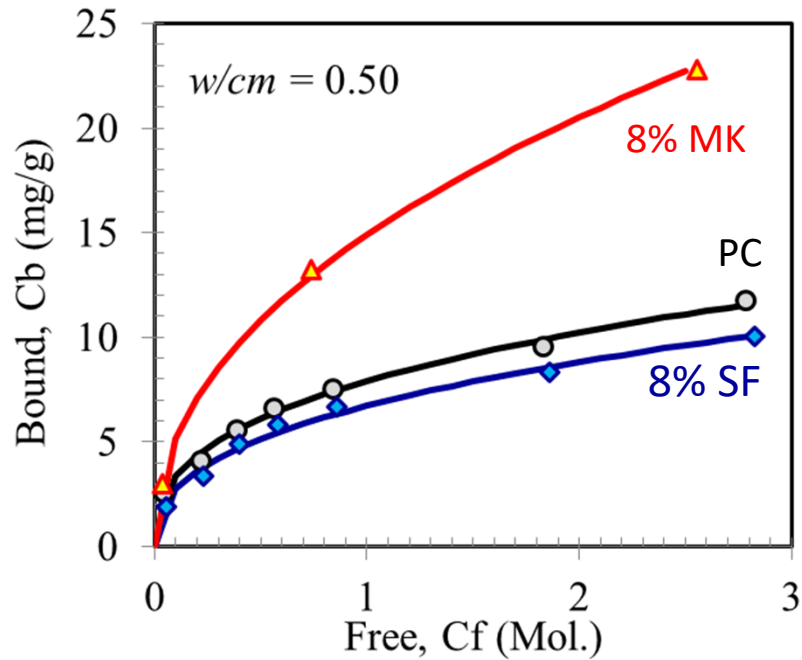


Comparison of Predicted vs Measured Values

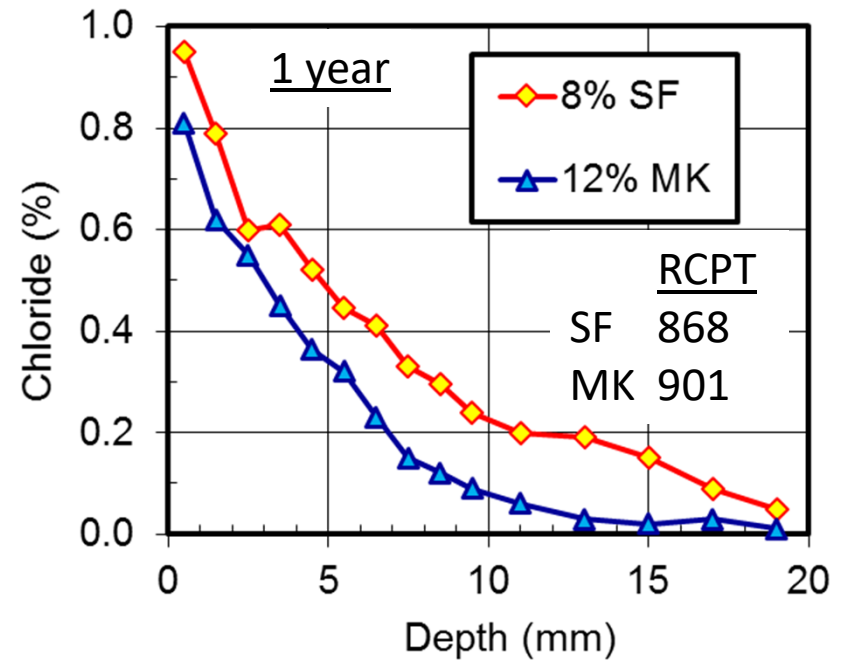
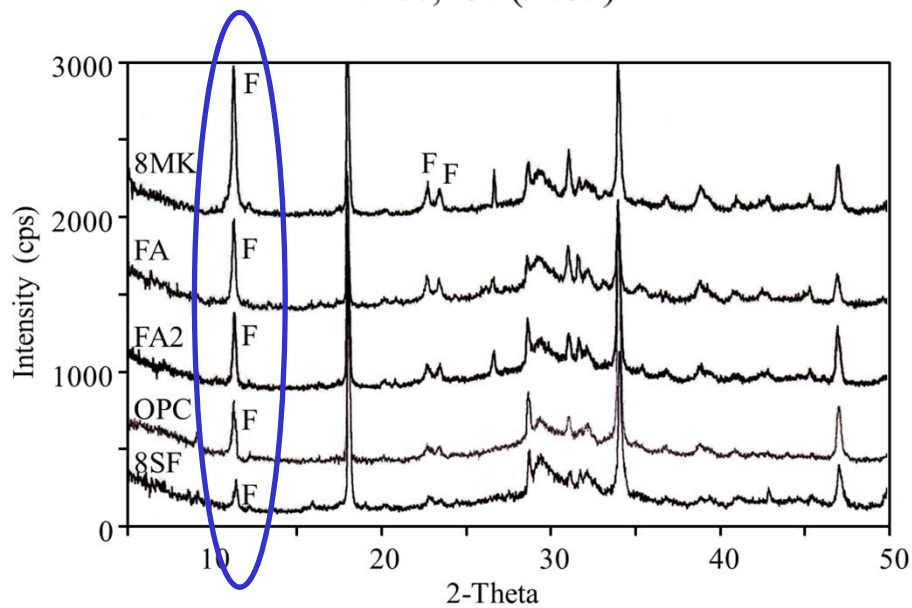
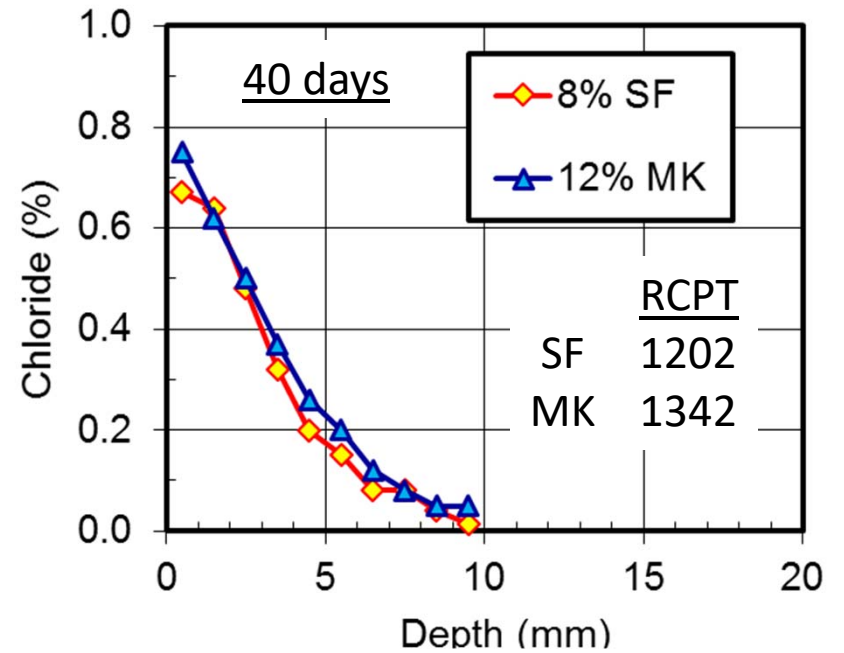
- Measurements made on pore solution pressed from hardened paste samples at 90 days
- Predictions made using NIST - <https://ciks.cbt.nist.gov/poresolncalc.html>



Metakaolin vs. Silica Fume



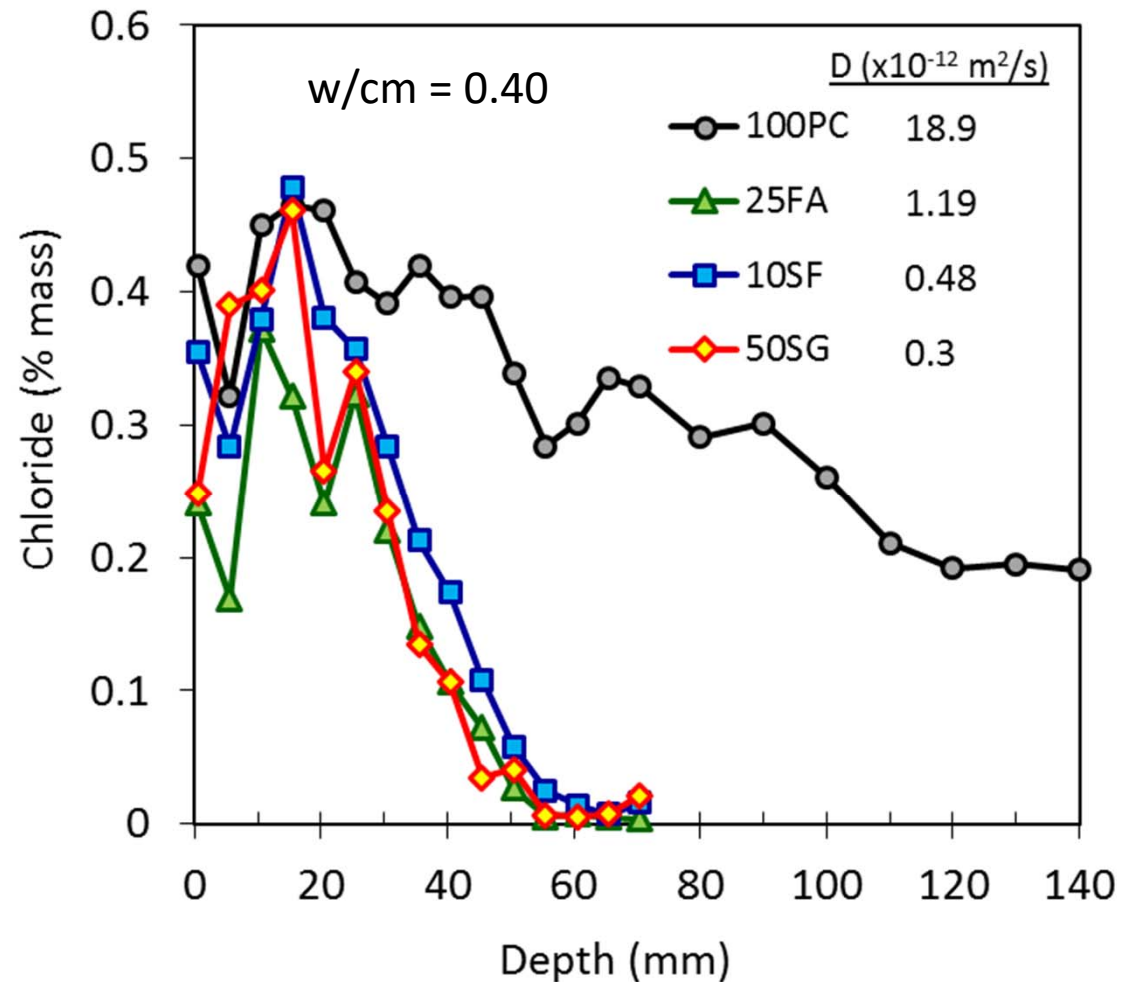
Bulk Diffusion Tests (C 1556)





Concrete Blocks (1 x 1 x 3 ft) at Treat Island in Tidal Zone for 25 years

Mix	Bulk ρ (K Ω .cm)	RCPT (Coulomb)
100PC	8.4	3050
25FA	23.2	1230
10SF	16.9	1630
50SG	29.7	905



A study of the effect of chloride binding on service life predictions

B. Martín-Pérez^{a,*}, H. Zibara^b, R.D. Hooton^b, M.D.A. Thomas^b

Cement and Concrete Research 30 (2000) 1215–1223

No binding: $C_b = 0$ $\frac{\partial C_b}{\partial C_f} = 0$ $D_c^* = D_c$

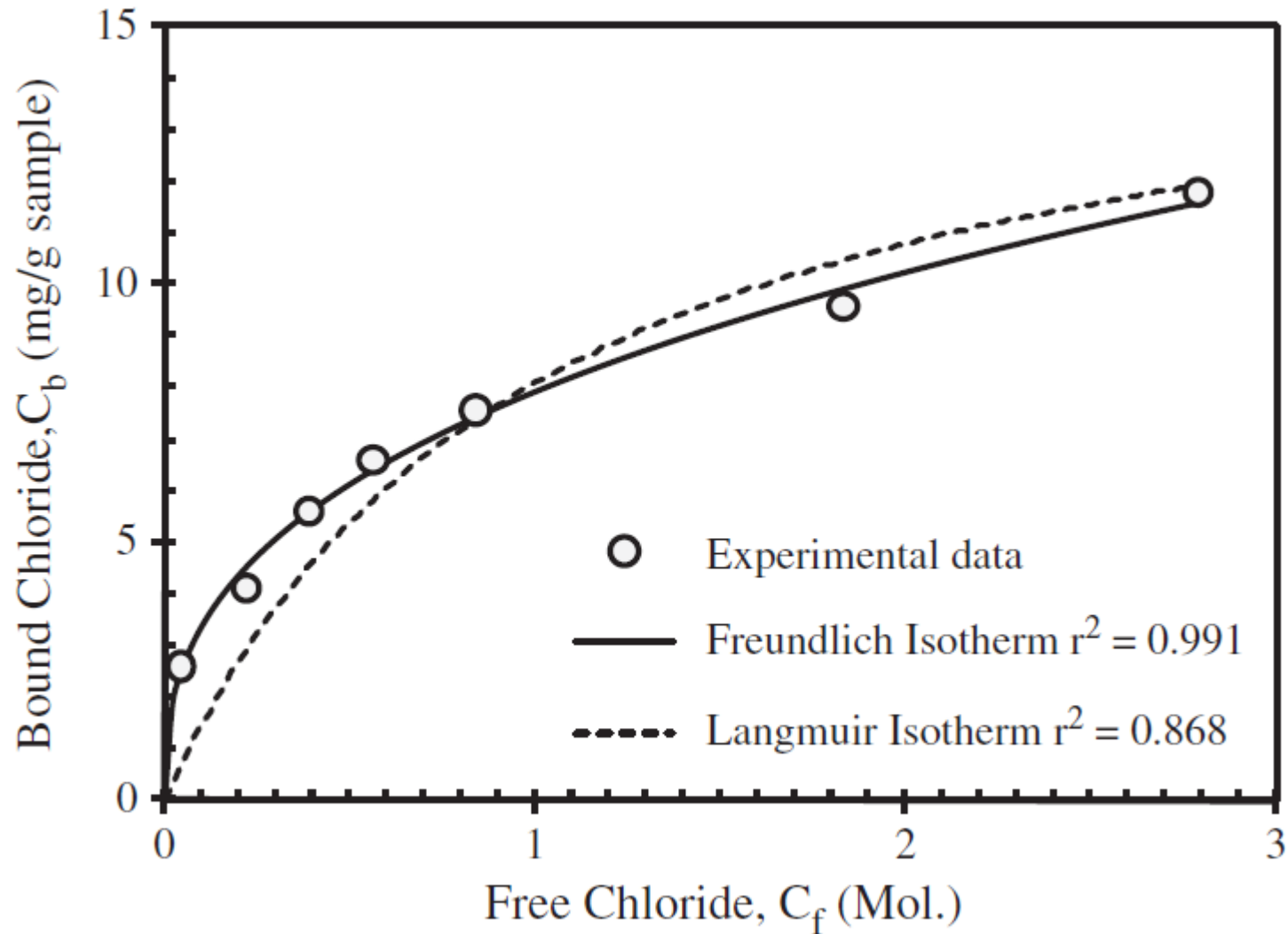
Linear isotherm: $C_b = \alpha C_f$ $\frac{\partial C_b}{\partial C_f} = \alpha$ $D_c^* = \frac{D_c}{1 + \frac{\alpha}{\omega_e}}$

Langmuir isotherm: $C_b = \frac{\alpha C_f}{1 + \beta C_f}$ $\frac{\alpha C_b}{\alpha C_f} = \frac{\alpha}{(1 + \beta C_f)^2}$ $D_c^* = \frac{D_c}{1 + \frac{\alpha}{\omega_e (1 + \beta C_f)^2}}$

Freundlich isotherm: $C_b = \alpha C_f^\beta$ $\frac{\partial C_b}{\partial C_f} = \alpha \beta C_f^{\beta - 1}$ $D_c^* = \frac{D_c}{1 + \frac{1}{\omega_e} \alpha \beta C_f^{\beta - 1}}$

The effect of supplementary cementitious materials on chloride binding in hardened cement paste
Cement and Concrete Research 42 (2012) 1–7

M.D.A. Thomas ^{a,*}, R.D. Hooton ^b, A. Scott ^c, H. Zibara ^b



The effect of supplementary cementitious materials on chloride binding in hardened cement paste
Cement and Concrete Research 42 (2012) 1–7

M.D.A. Thomas ^{a,*}, R.D. Hooton ^b, A. Scott ^c, H. Zibara ^b

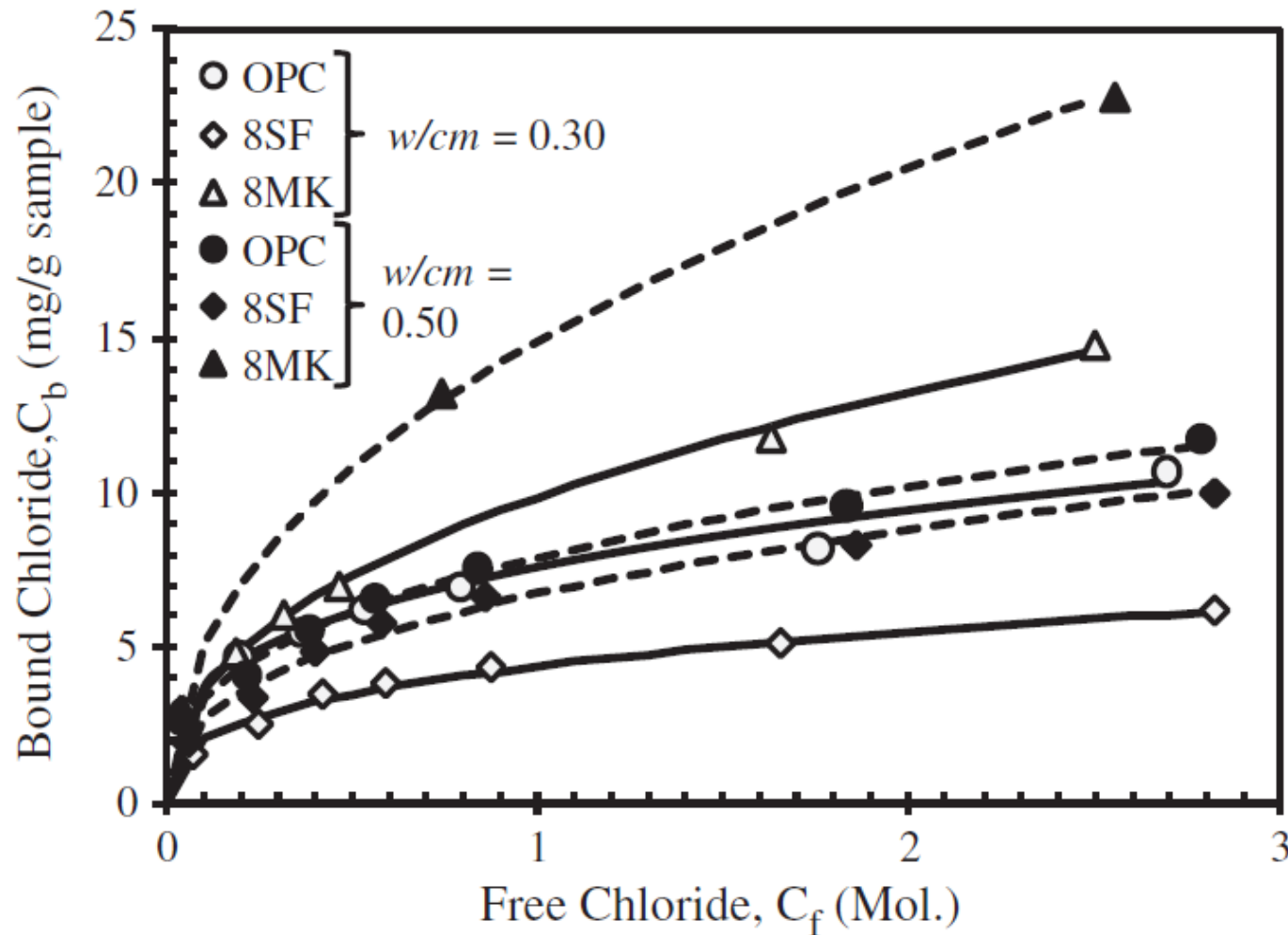
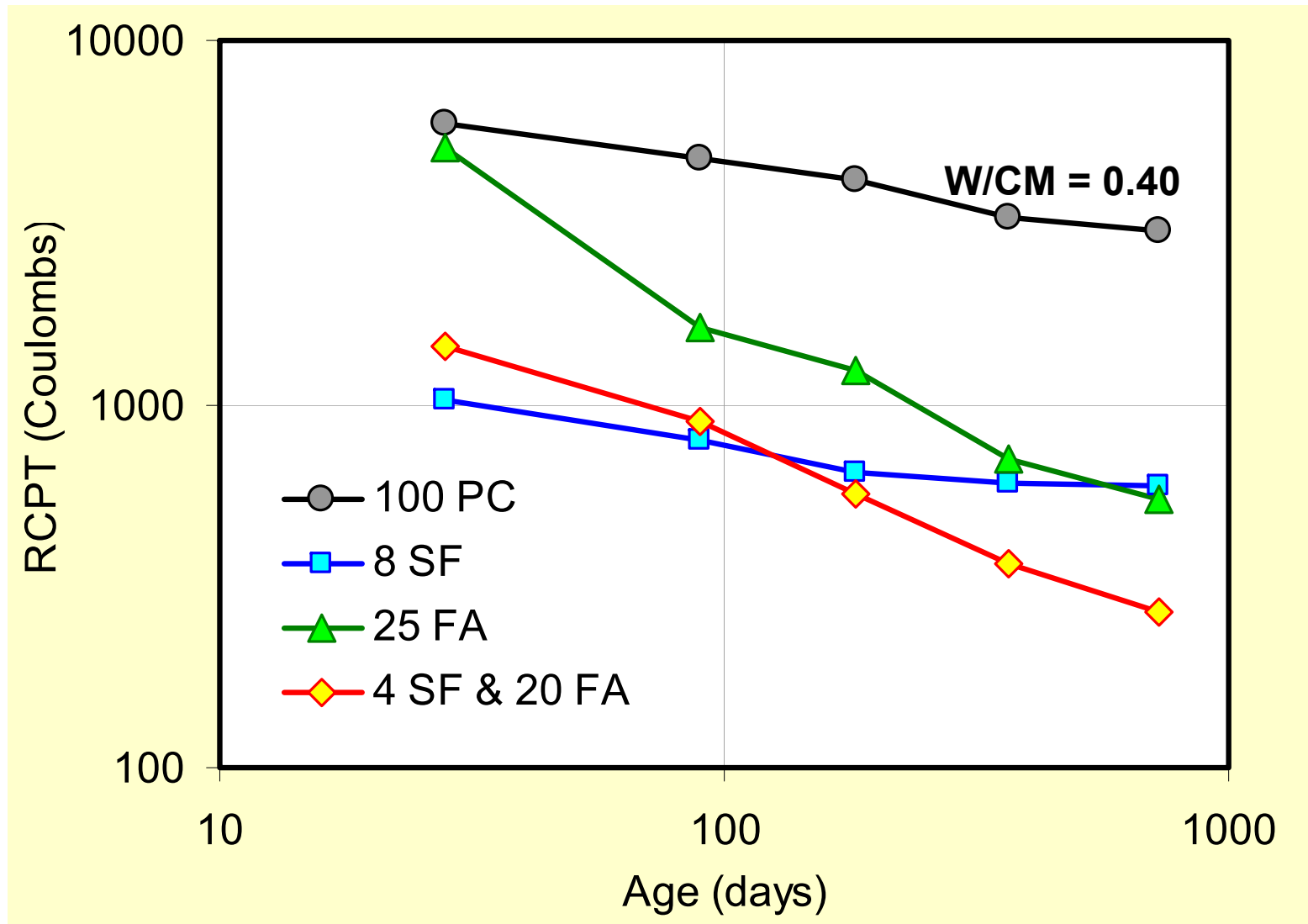
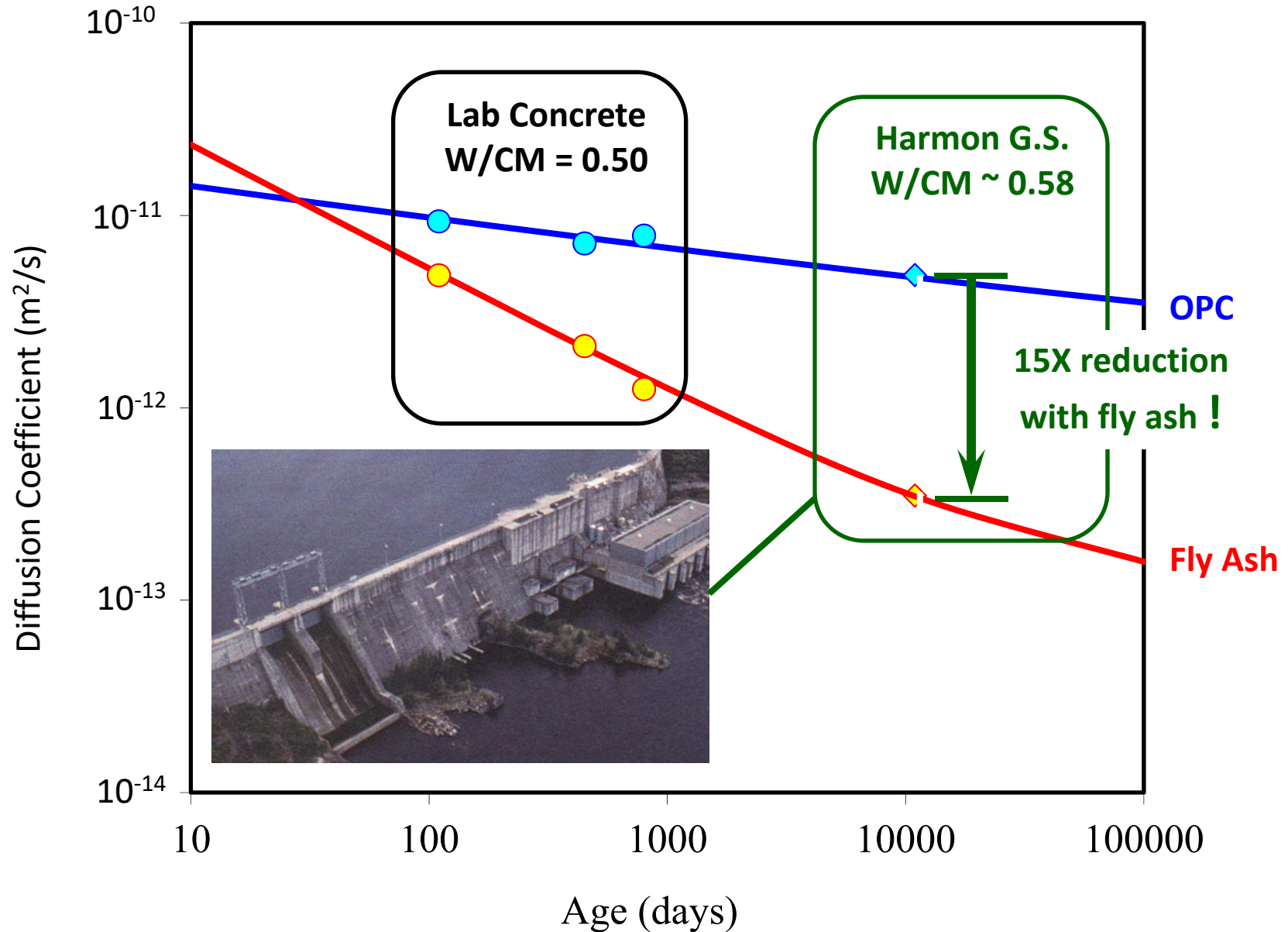


Fig. 3. Chloride binding isotherms for pastes with silica fume and metakaolin ($w/cm = 0.30$ and 0.50 , $T = 23$ °C).

Time-Dependent Changes in Electrical and Transport Properties



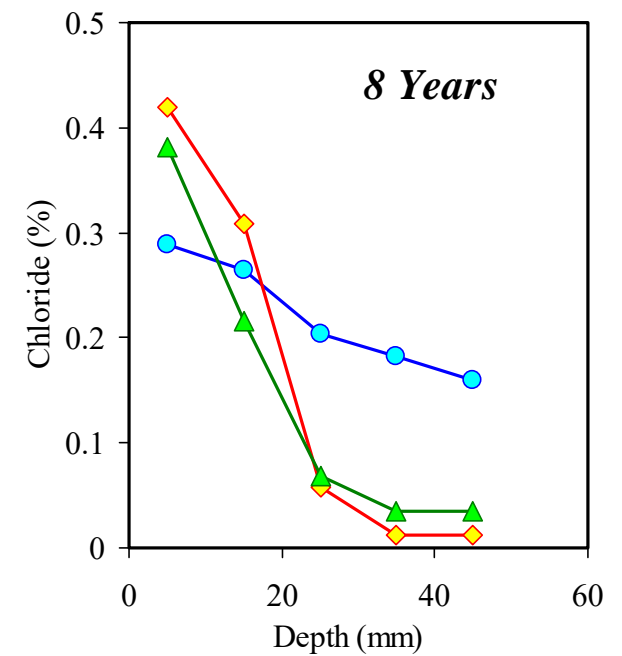
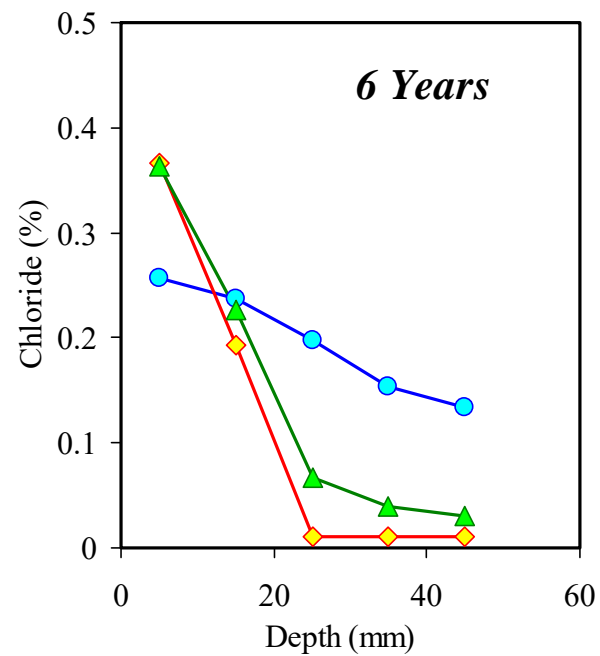
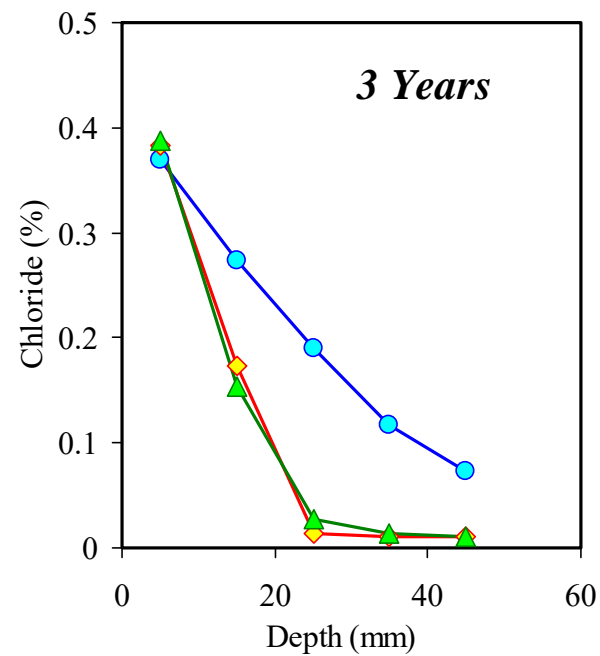
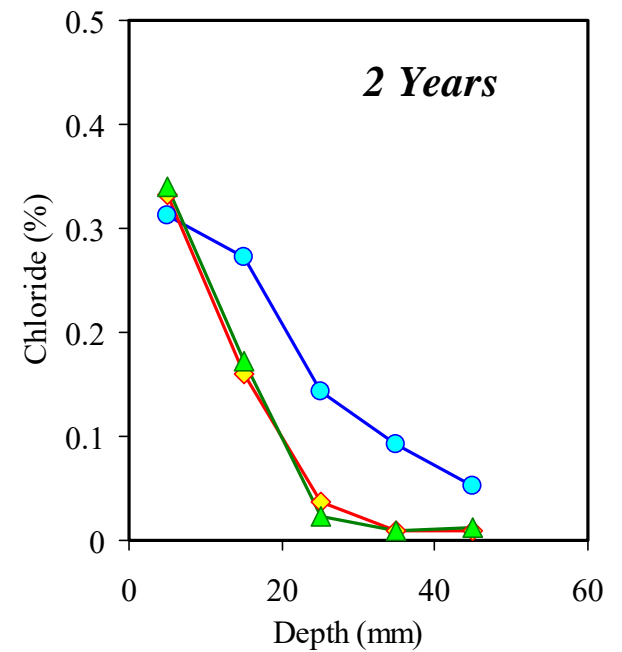
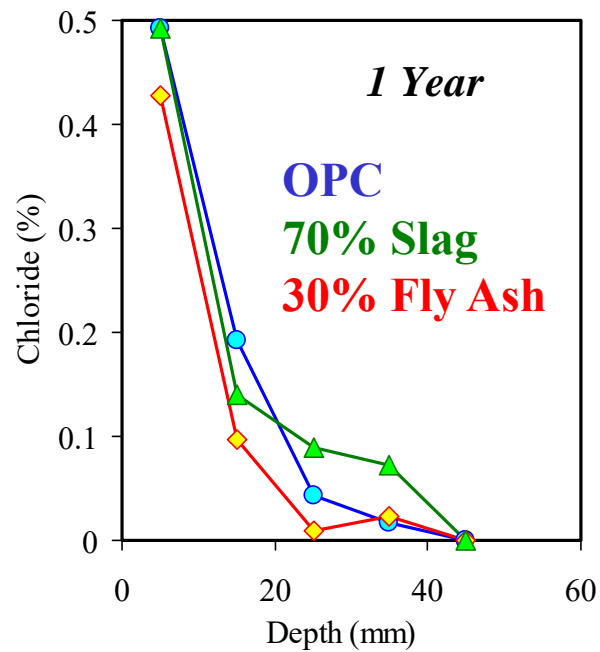
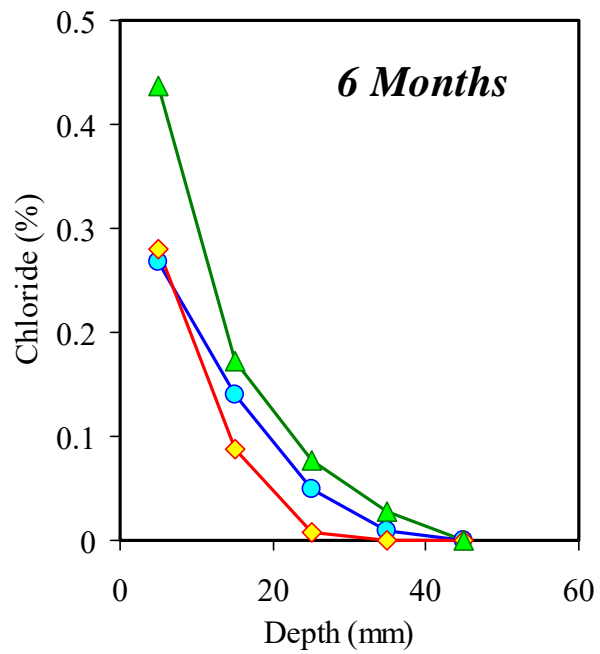
Bulk Diffusion (ASTM C 1556) Results for Lab & Field Concretes

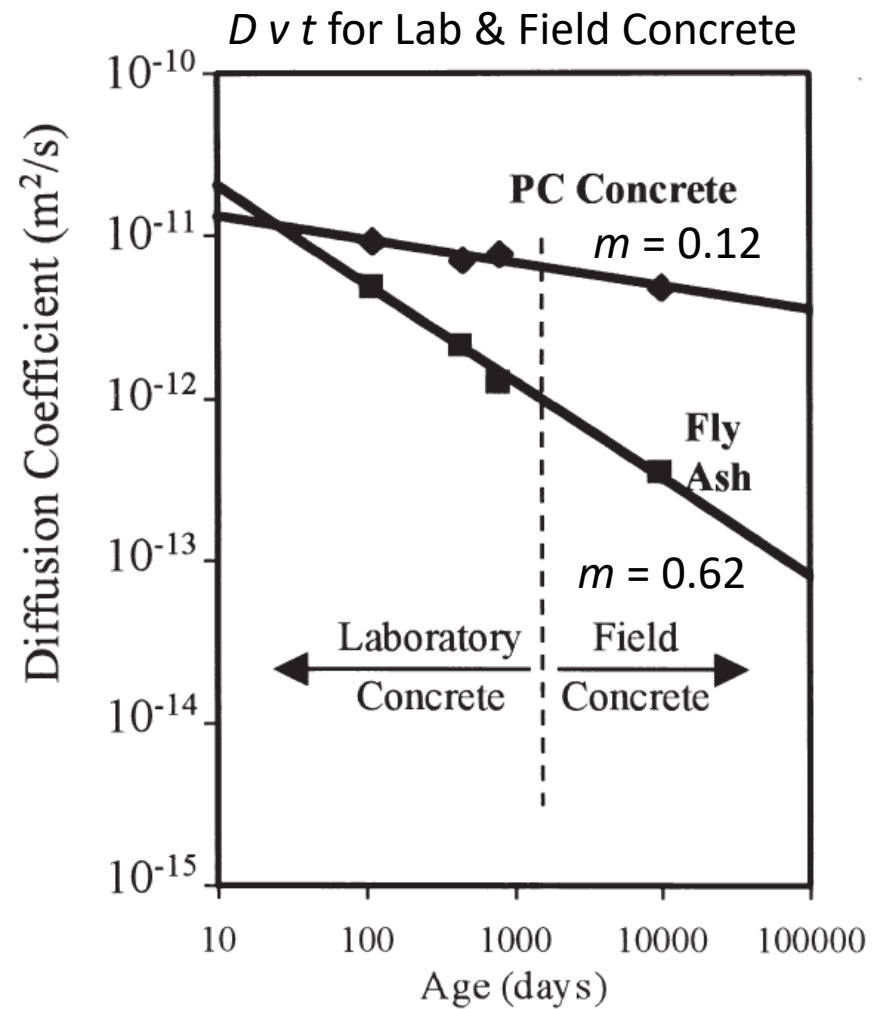
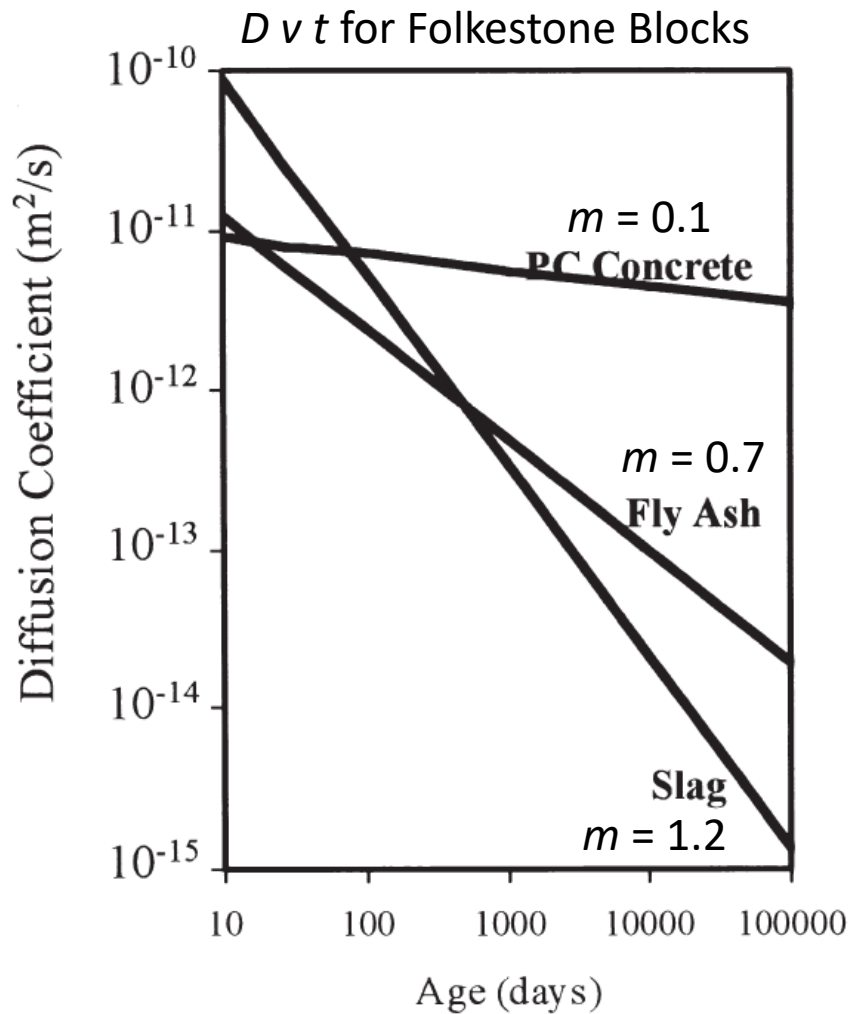


Taywood Blocks nr. Folkestone



Thomas & Bamforth, 1999





Conclusions

- Electrical resistivity/conductivity provides a good indication of the mass-transport properties of Portland-cement concrete
- The relationship between electrical and mass-transport properties of concrete is strongly influenced by a number of parameters including pore-solution conductivity
- Predicting or measuring the pore-solution conductivity is **not** trivial
- Electrical properties do **not** account for the interaction between chlorides and the hydrates (binding) and this can be a **very** significant factor for some binders
- Early-age measurements of either electrical or mass-transport properties do **not** capture the substantial changes that may occur with high replacement levels of pozzolans or slag

Questions?

