

Transport Properties
Electrical Measurements

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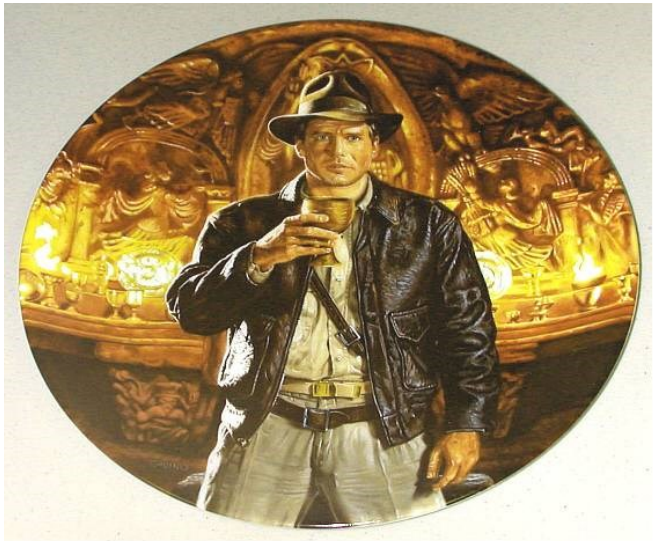
Where Do We Find Tests

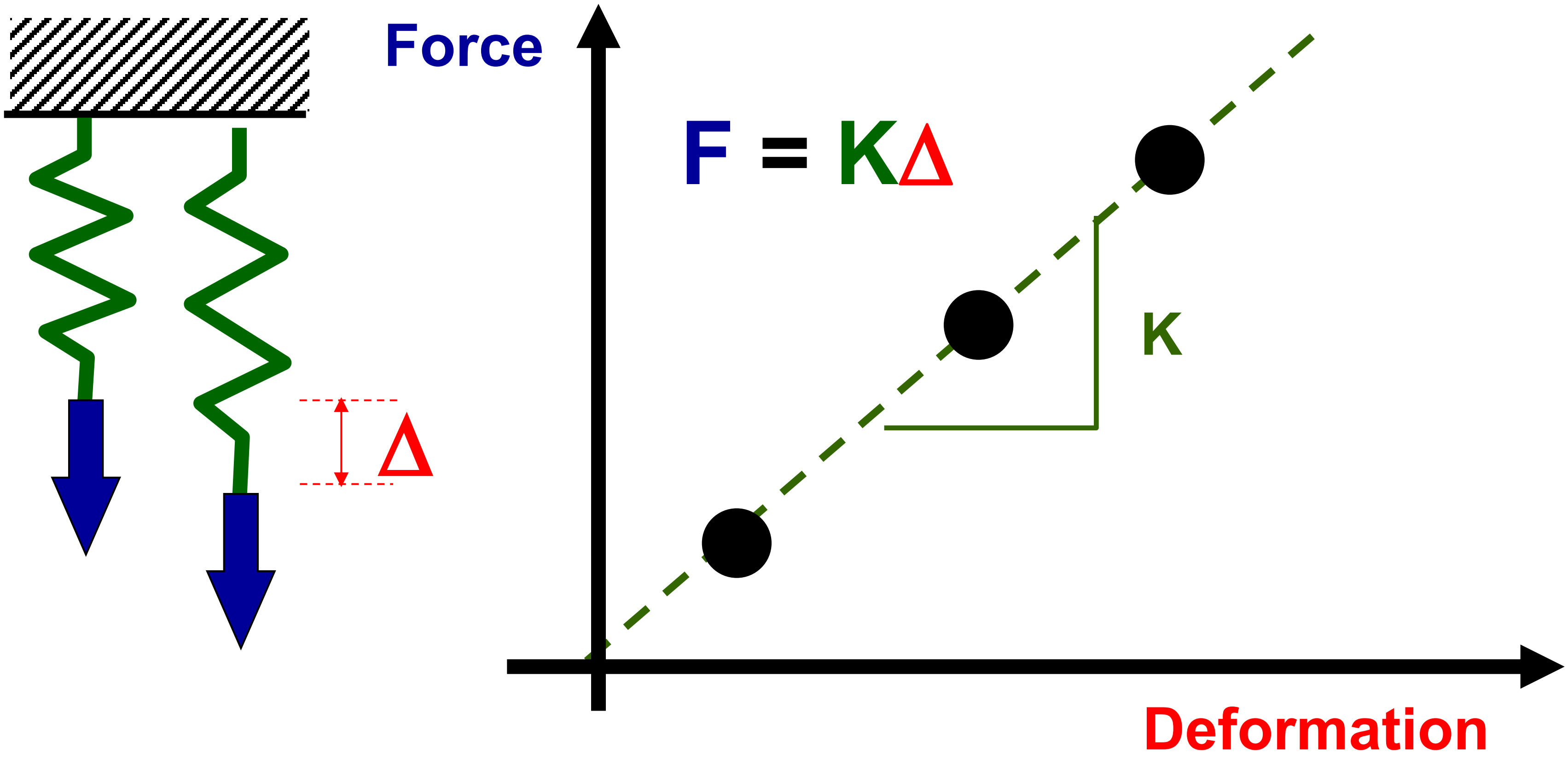
σ, ρ
Geometry
3 Factors
Pore soln
Porosity
Tortuosity
Variability
Saturation
Temperature
Leaching
Acceleration
Field Use



- Much like Indiana we seem to be on the impossible search for the "holy grail"
- We want a test for transport (or durability) that is fast, accurate, inexpensive easy to interpret but it also needs to be scientifically valid
- We think that electrical measurements can be a significant part of this approach

Recall Many Physical Relations

- Recall the relationship between load and deformation



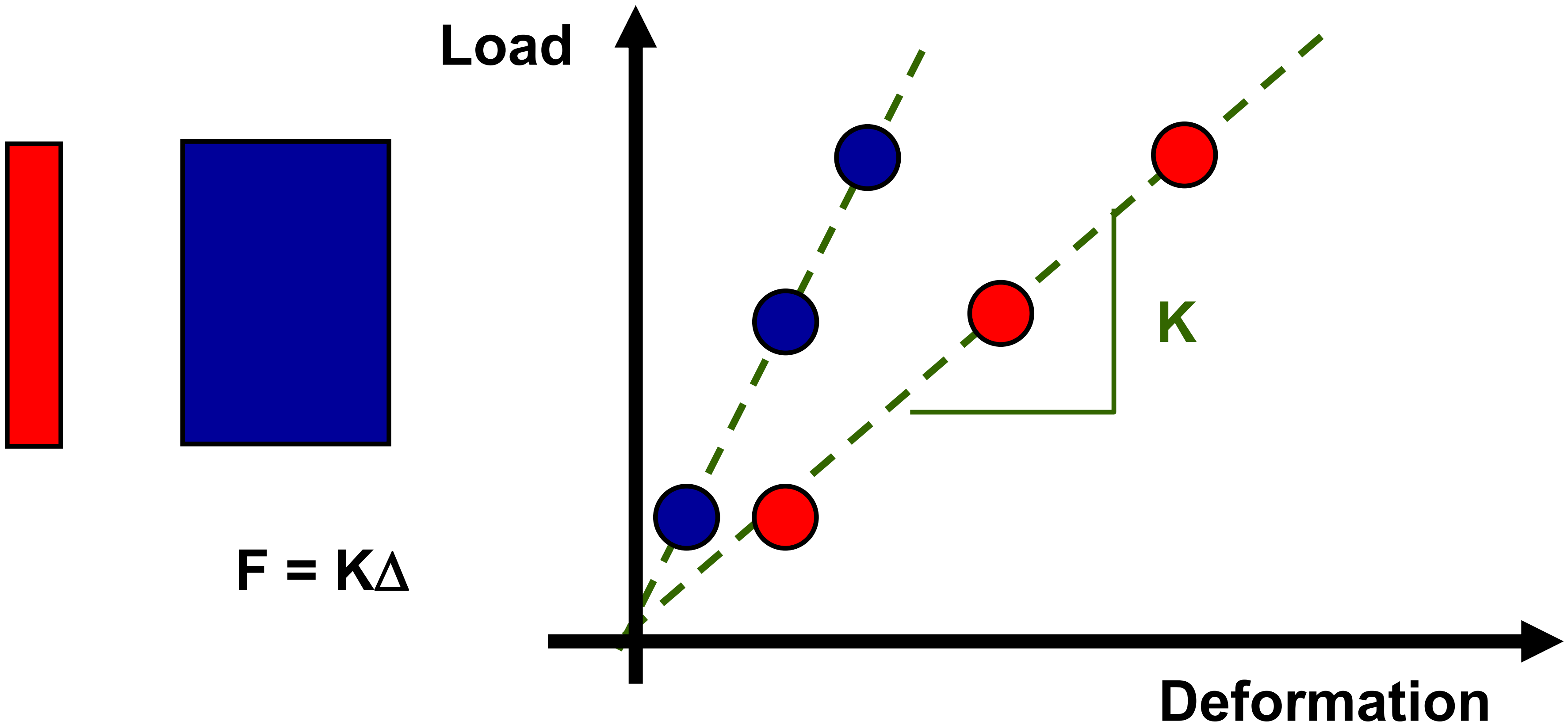
George Ohm

- German physicist
- Defined fundamental relationships of voltage, current and resistance
- Inspired by Fouriers work on heat conduction
- German Minister of Education proclaimed "a professor who preached such heresies was unworthy to teach science."

Henry Cavendish

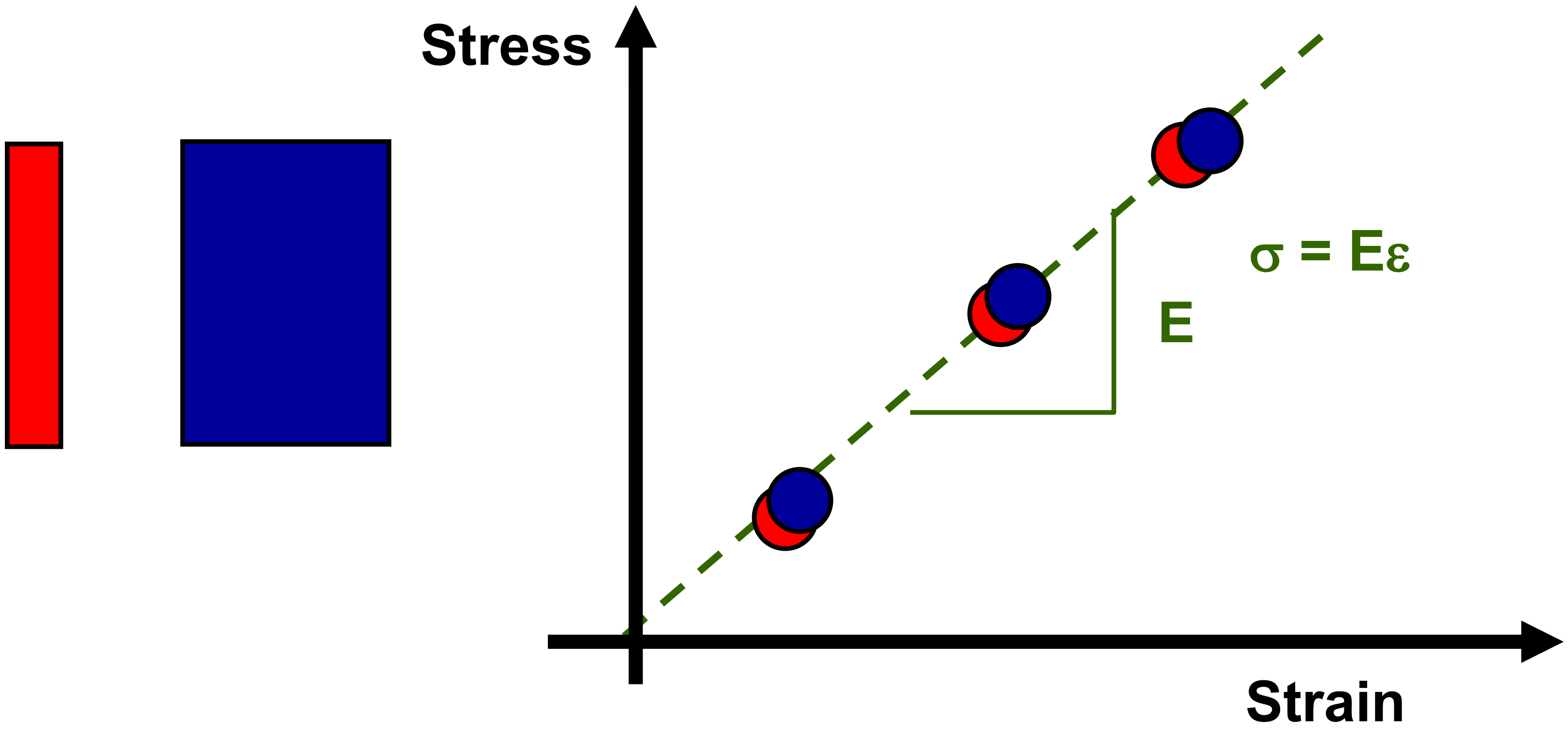
- British Scientist
- Silent, solitary, shy
- Discovered Hydrogen – Lavoisier 'named'
- Discovered Ohms Law later identified when Maxwell went through his papers

Does Stiffness Vary Depending on Size



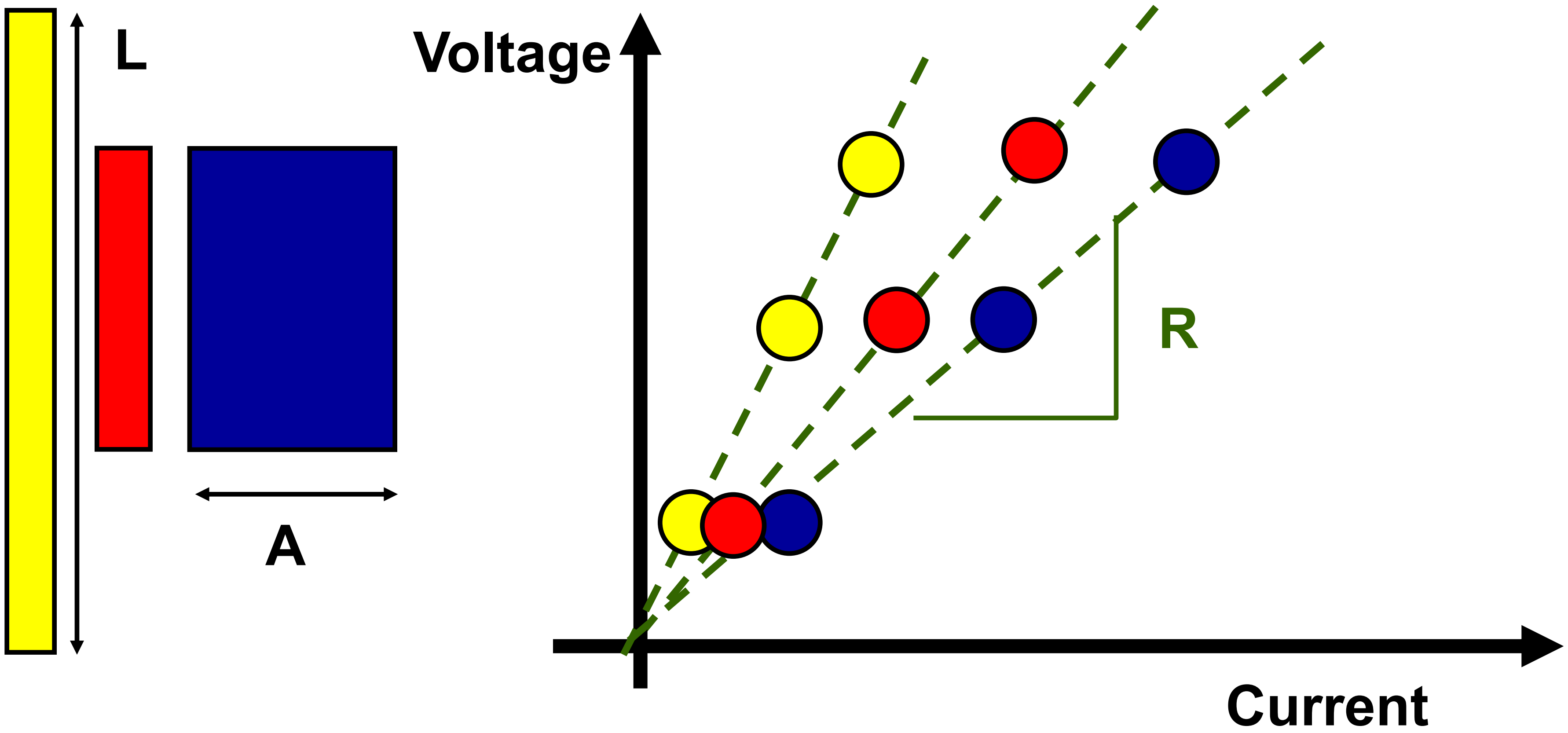
Instead of Stiffness We Use Elastic Modulus

- Is resistance a material property?



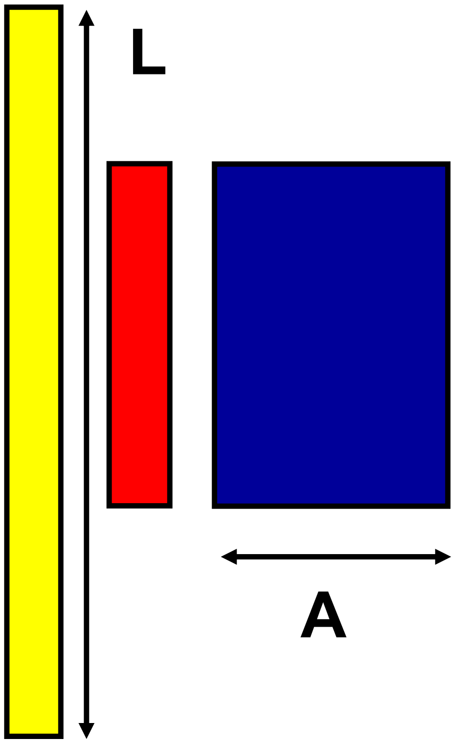
Electrical Resistance

- Is resistance a material property?

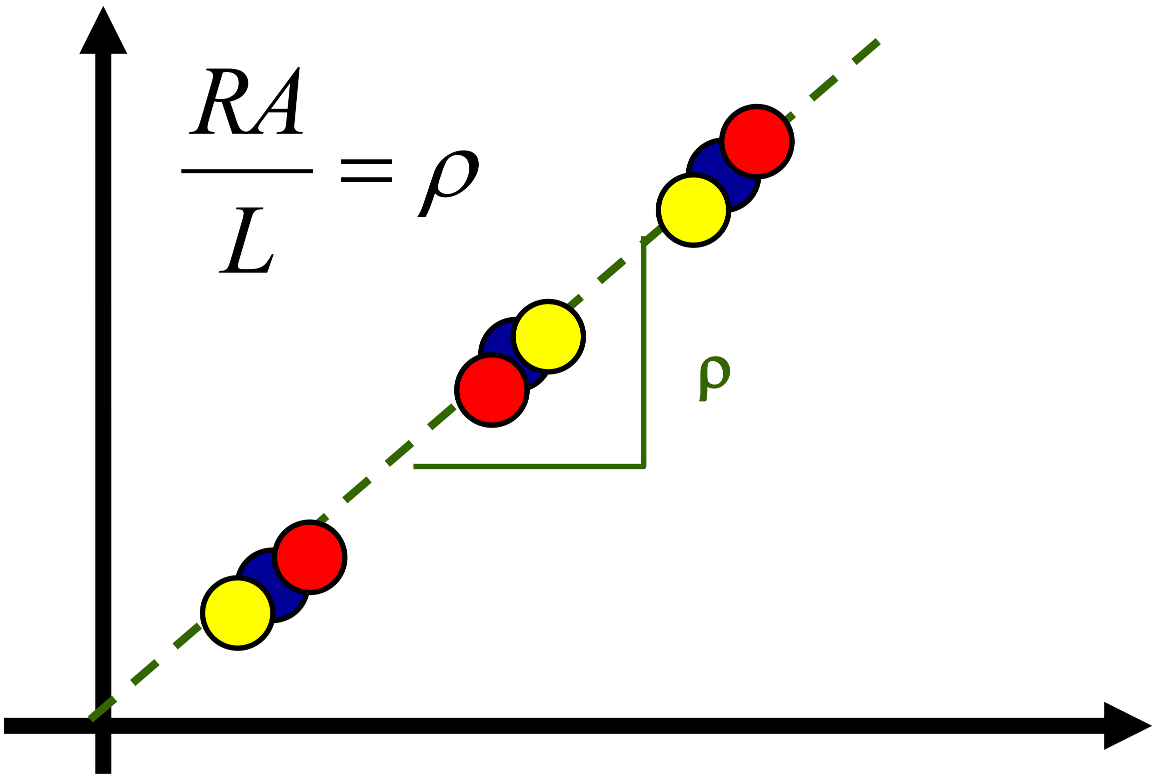


Electrical Resistance

- Is resistance a material property?



$$\frac{RA}{L} = \rho$$



Conductivity and Other Geometries

$$\sigma = \frac{1}{\rho} = \frac{k}{R}$$

Geometry Factor (1/m) → k

Resistance (Ω) → R

Resistivity (Ωm) → ρ

Conductivity (S/m) → σ

Interchangeable, I find σ easier to think about, however practice seems to like ρ, so be it

Rapid Test Methods

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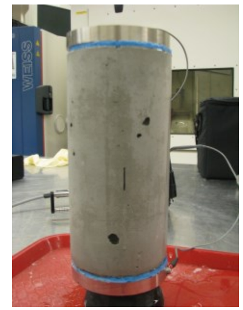
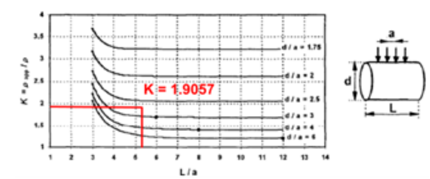
Field Use

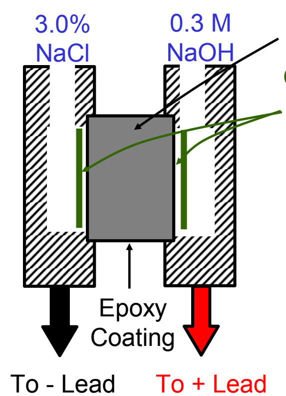
- Uniaxial, surface, embedded, and RCPT electrical measurements all yield results that can be directly compared if done properly
- Proper reporting is essential



$$\rho = \frac{V}{I}\frac{A}{L} = \frac{RA}{L}$$

$$\rho = \frac{V}{I} \cdot 2\pi a \cdot \kappa$$

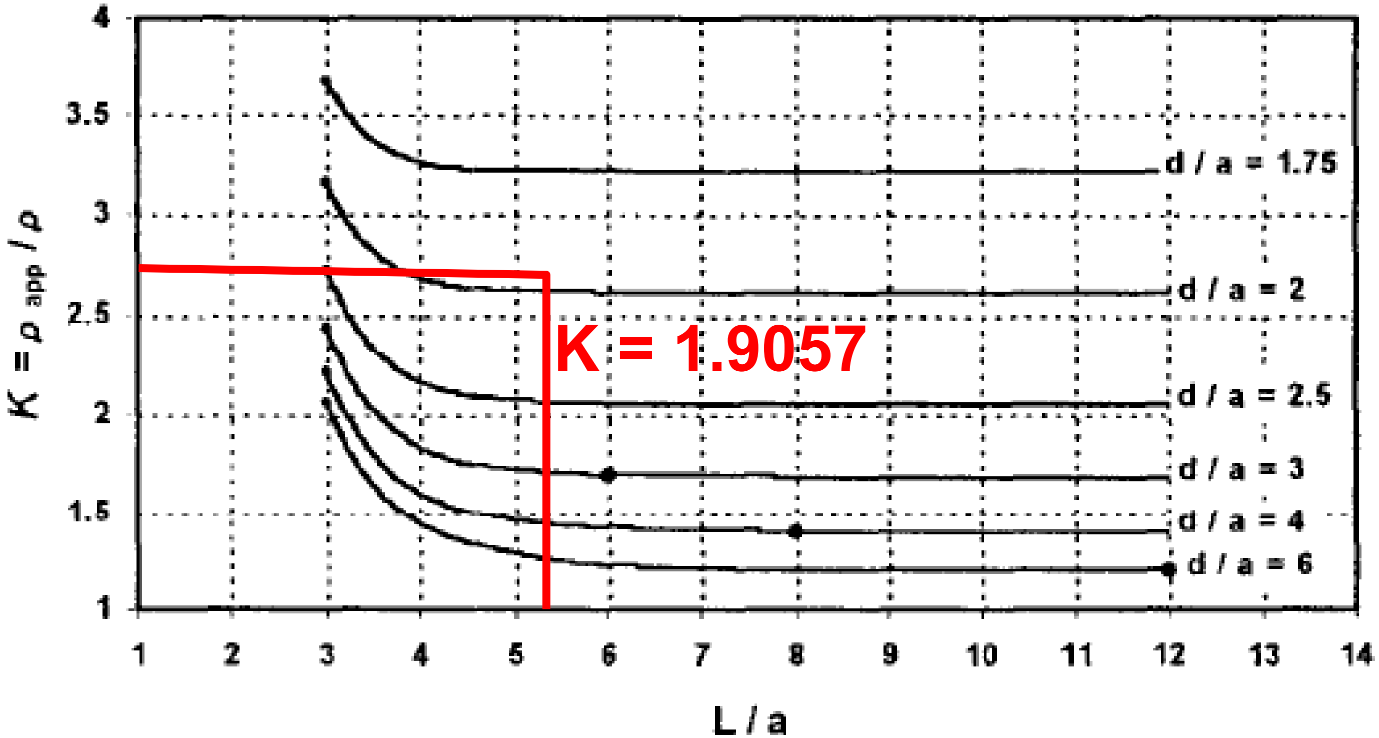


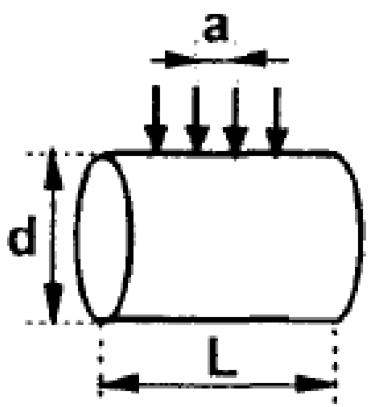


$$Q = \int_{0h}^{6h} \frac{V}{\rho\kappa} dt$$

Geometry Factor

- Recall the need for a geometry factor
- 4 x 8 cylinder; a = 1.5 in
- L/a = 8/1.5 = 5.26   d/a = 4/1.5 = 2.63





RCPT Analyzed

- Coloumb = Amp – Sec
- I = Coloumb / (6 hr * 60 min/hr *60 sec/min)
- V = 60 V
- V = I R
- R = V / I

$$Q = \int_{0h}^{6h} \frac{V}{\rho \kappa} dt$$

RCPT	Current	Voltage	Resistance
Coulombs	Amps	V	K-Ohms
6000	0.278	60	0.22
5000	0.231	60	0.26
4000	0.185	60	0.32
3000	0.139	60	0.43
2000	0.093	60	0.65
1000	0.046	60	1.30
500	0.023	60	2.59
100	0.005	60	12.96

Relationship Between Q (Coloumbs) and Resistivity (ρ)

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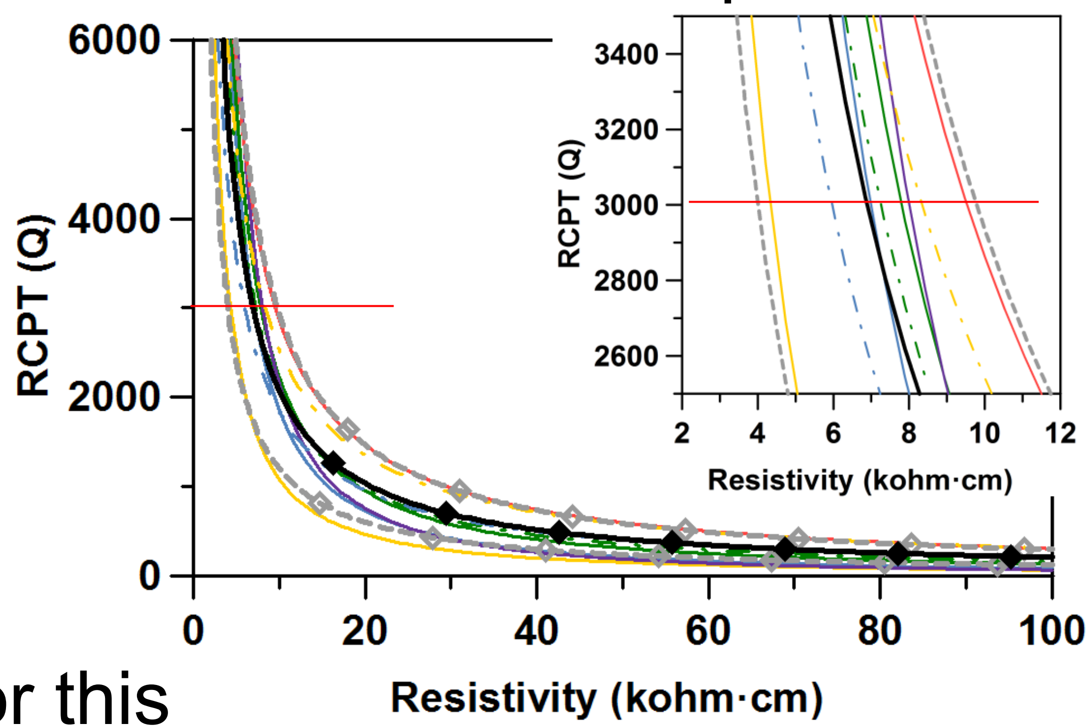
Field Use

- Many relationships have been developed over the years (the black - theory) $Q = \int_{0h}^{6h} \frac{V}{\rho\kappa} dt$
- While all have a reasonable shape, details are very important when one tries to use this in spec's
- Explored reasons for this

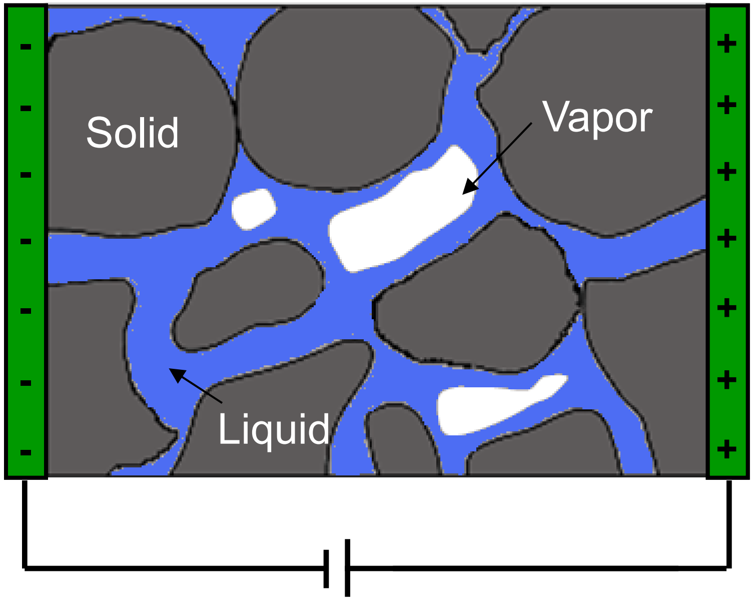


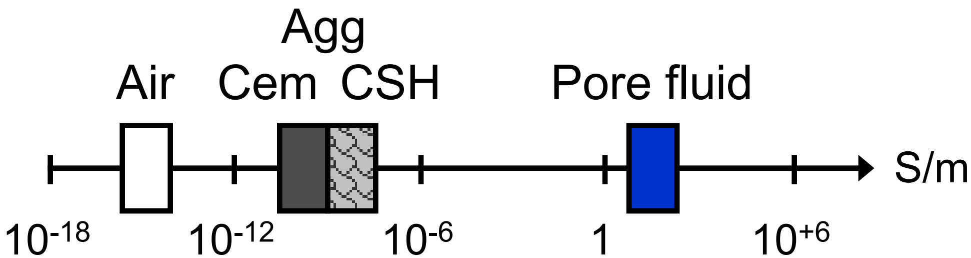
Spragg et al. 2013

Mechanism of Electrical Conduction in Concrete

Concrete is a composite:

- Solid phase (unhyd Cement, CSH, CH,…); $\sigma_{sol} \approx 10^{-9}$ S/m
  (Rajabipour 2006 based on results of Hammond and Robson 1955)
- Liquid phase (pore solution);
  $\sigma_{liq} \approx 1$ S/m to 20 S/m
  (Christensen 1993)
- Vapor phase (air voids, emptied pores); $\sigma_{vap} \approx 10^{-15}$ S/m
  (Aplin 2005)





Flow of electricity is essentially ionic and through material's liquid phase

Modified Parallel Law to Model Concrete Conductivity

- Considers pore fluid as the only conductive phase in concrete
- Pore fluid can be in capillary or gel pores or in aggregate pores

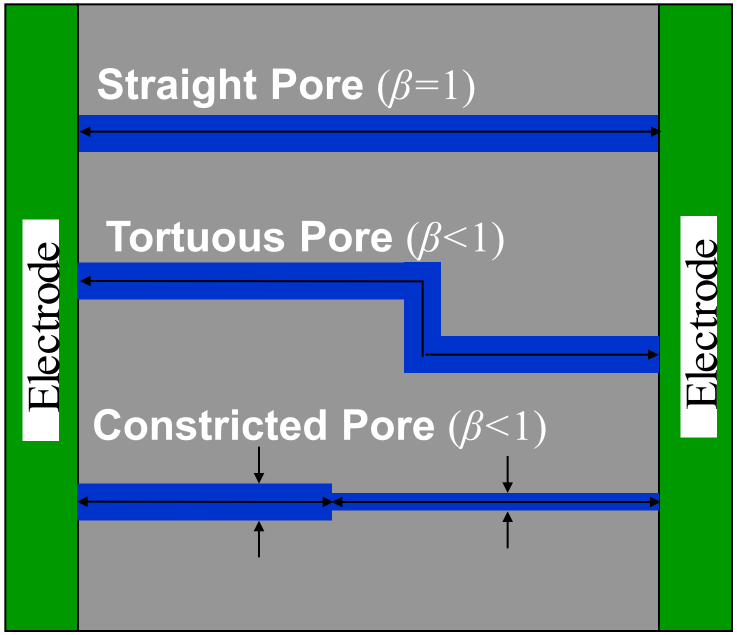
$$\sigma_t = \sigma_o \phi \beta$$

σ_t: concrete conductivity (S/m)

σ_o: pore solution conductivity (S/m)

ϕ: liquid volume fraction

β: avg. liquid connectivity (describes liquid tortuosity and constrictedness)



(Garboczi 1990, Christensen et al. 1994, Rajabipour 2006)

Electrolyte

σ, ρ
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Field Use

- Gatorade
- 90 million in royalties to university of florida
- Helps with dehydration maybe even a hangover
- Imbalance of extracellular and interstitial fluid
- Discovered in 1965

An Electrolyte

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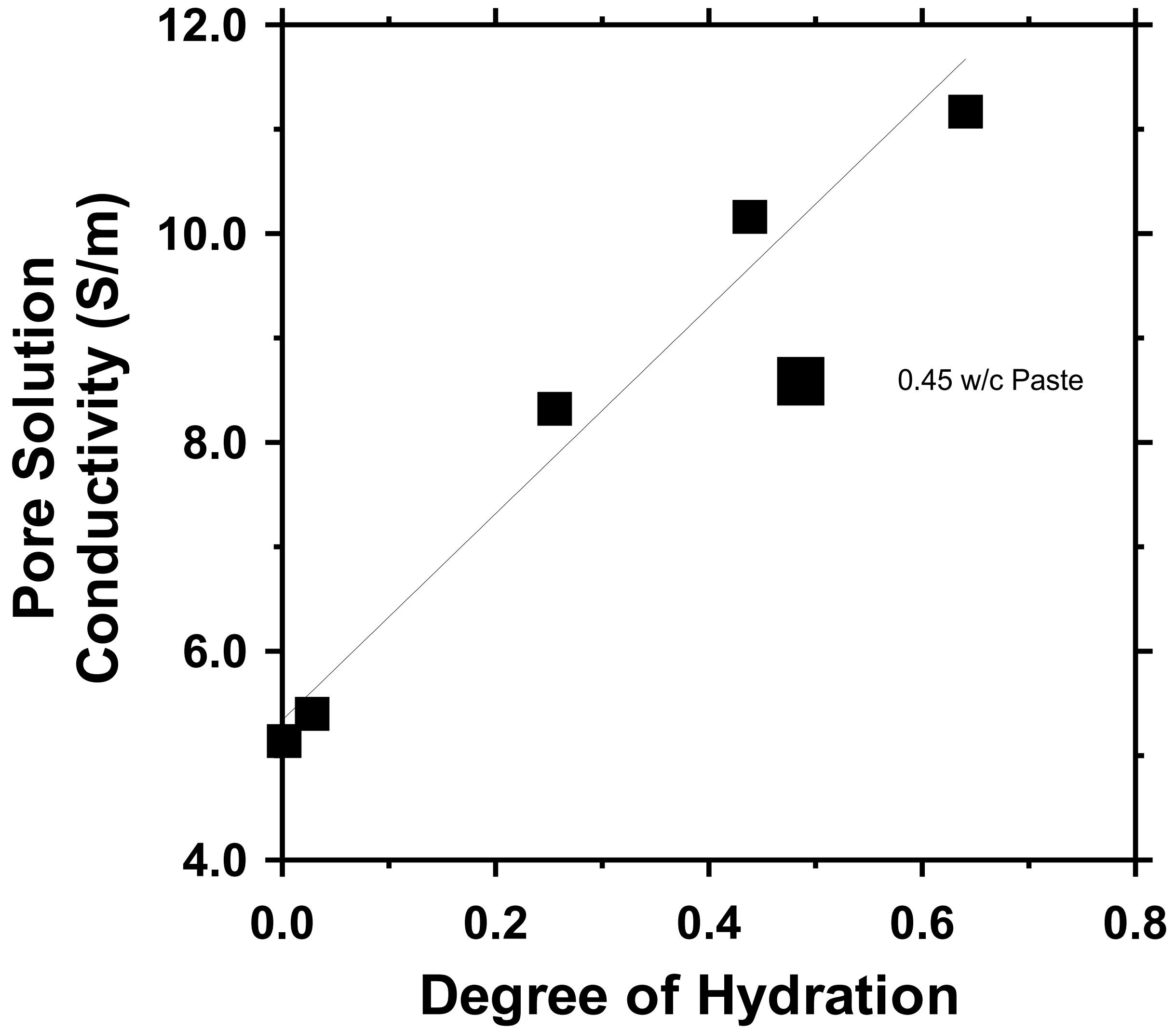
Field Use

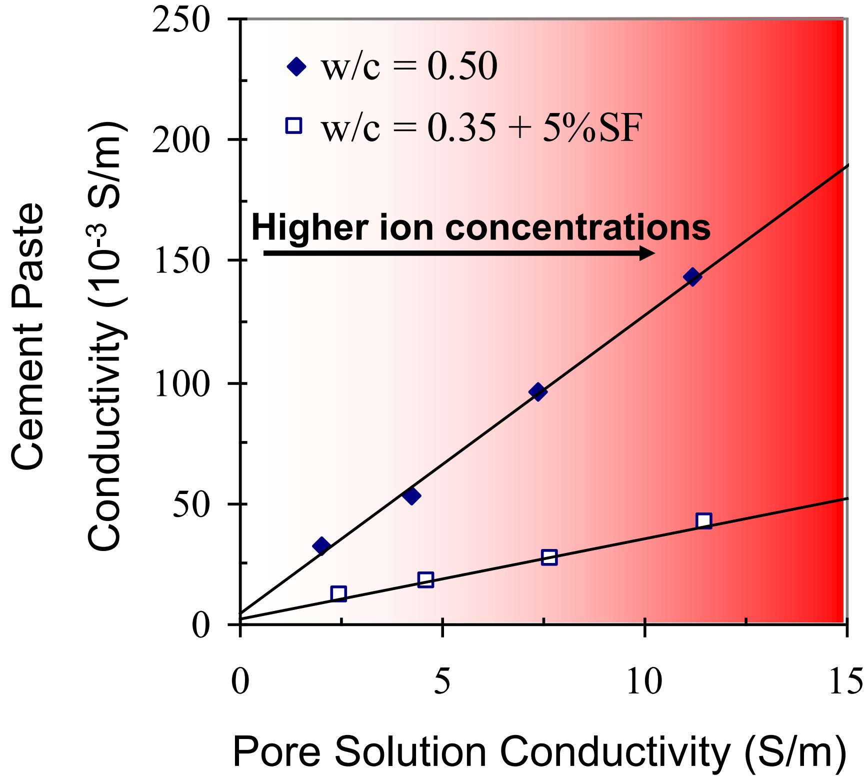
- Contains free ions making it electrically conductive (mostly liquids though solids exist)
- Solutions of acids, bases or salts
- Typically form when a salt is place in a solvent and individual components disassociate due to solvation
- Sodium chloride in water
- Concentrated with high number if ions
- Na^+, K^+, $Ca^{2+,}$ Mg^{2+}, Cl^-, HPO_4^{2-}, HCO_3

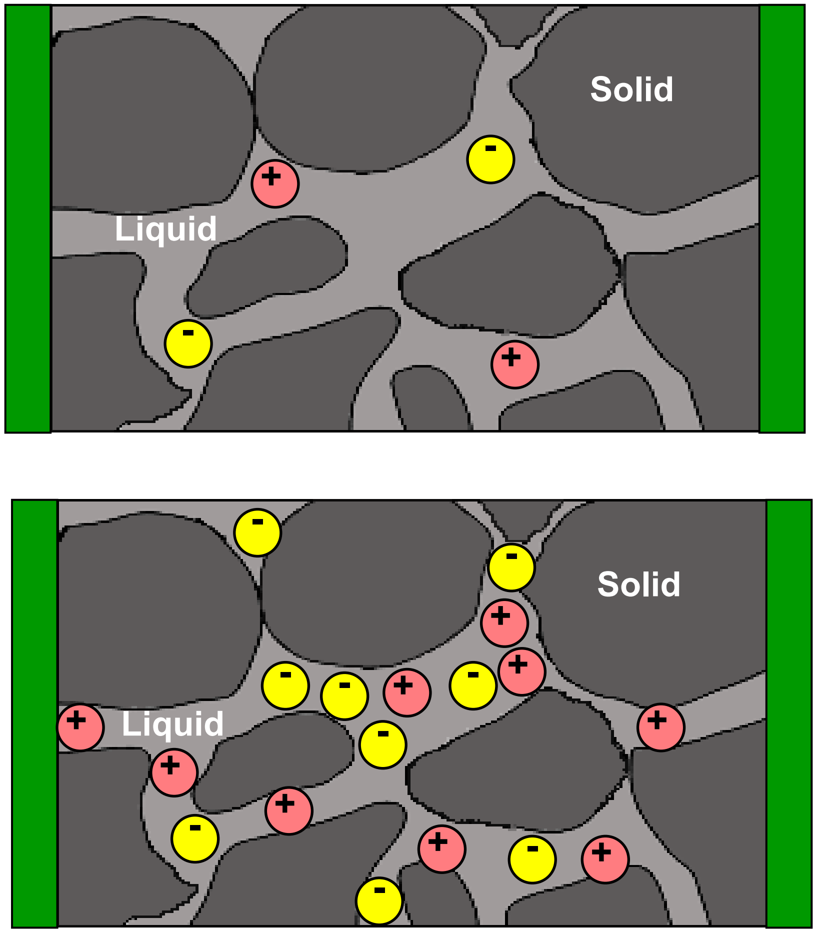
Pore Solution Conductivity

- Linearly proportional to the DOH
- Pore fluid volume is estimated from Powers or measured with drying



Pore Fluid Composition





$$\sigma_t = \sigma_o \phi \beta$$

NIST Model

Estimation of Pore Solution Conductivity

The purpose of this form is to provide an estimate of the electrical conductivity (S/m) of the pore solution in a concrete based on the mixture proportions and achieved degree of hydration.

It is assumed that 75 % of the sodium and potassium initially present as oxides in the cement-based materials will be released into the pore solution. In the presence of silica fume, more alkalies are absorbed by the products of the pozzolanic reactions and "free" alkali ions are further reduced. This calculation onl considers the alkali ions and their accompanying hydroxides and not others such as chlorides, etc.

Mixture Proportions

Material	Mass (kg or lb)	Na_2O content (mass %)	K_2O content (mass %)	SiO_2 content (mass %)
Water	160.0	Not applicable	Not applicable	Not applicable
Cement	400.0	0.2	1.0	Not applicable
Silica fume	20.0	0.2	0.2	99.0
Fly ash	0.0	0.2	0.2	50.0
Slag	0.0	0.2	0.5	Not applicable

Estimated system degree of hydration (%): 70

Hydrodynamic viscosity of pore solution relative to water: 1.0

Curing: Saturated ◉ Sealed ○

Compute **Estimated pore solution composition (M):**

K+: 0.0

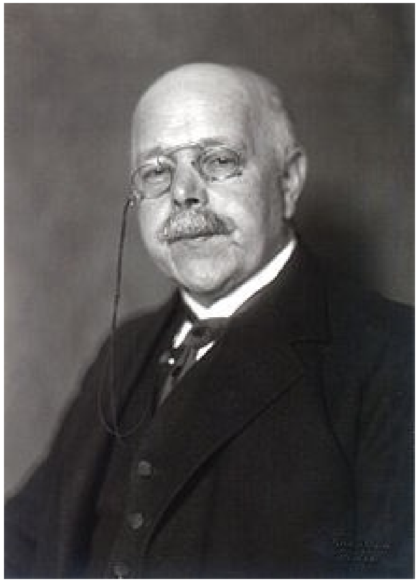
Na+: 0.0

OH-: 0.0

http://ciks.cbt.nist.gov/poresolncalc.html

Walther Nernst

- Walther Hermann Nernst (1864-1941)
- a German physical chemist and physicist who is known for his theories behind the calculation of chemical affinity
- he won the 1920 Nobel Prize
- establish field of physical chemistry and contributed to electrochemistry, thermodynamics
- known for developing the Nernst equation.



From Resistivity to Diffusivity Nernst Einstein Relationship

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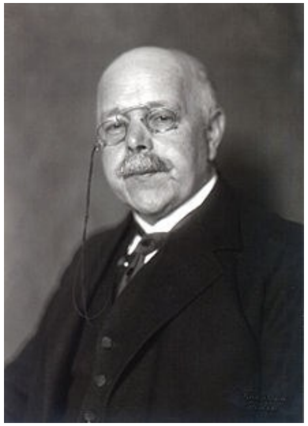
- Walther Nernst (1864-1941)
- German physical chemist/physicist
- Won1920 Nobel Prize

$$\frac{\sigma_t}{\sigma_o} = \frac{D_i}{D_i^{\mu}}$$



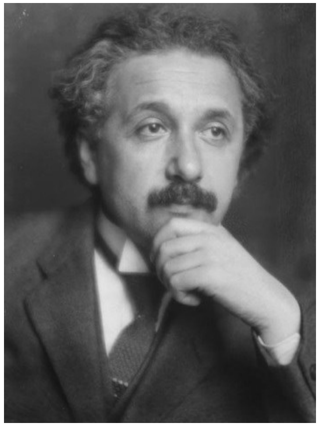


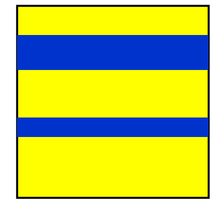
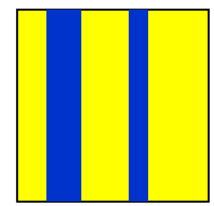
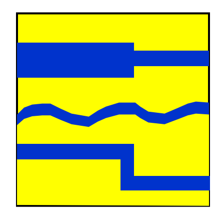
Table 1 – Diffusion coefficient of various species in free water	
Species	D_i^{μ} (10^{-9} m^2/s)
OH^-	5.273
Na^+	1.334
K^+	1.957
SO_4^{2-}	1.065
Ca^{2+}	0.792
Cl^-	2.032
Mg^{2+}	0.706

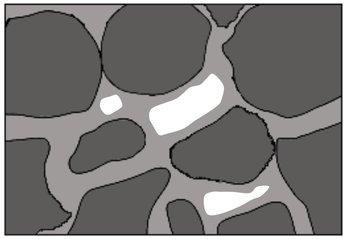
$$\frac{\rho_{Pore}}{\rho_{Bulk}} = \frac{D_i}{D_i^{\mu}} = \frac{1}{F}$$

$$D_i = D_i^{\mu} \cdot \frac{\rho_{Pore}}{\rho_{Bulk}}$$

$$D_i = D_i^{\mu} \cdot \phi\beta = D_i^{\mu} \cdot \frac{1}{F}$$

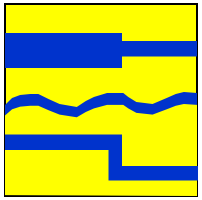
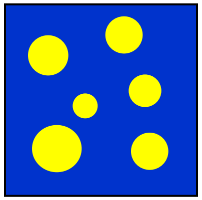
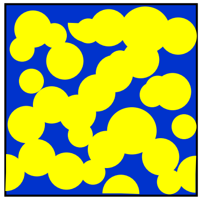
Simple Composite Models

NAME	FORMULA	MICROSTRUCTURE
Parallel	$D_{bulk} = D_1\phi_1 + D_2\phi_2$	
Series	$1/D_{bulk} = (\phi_1/D_1) + (\phi_2/D_2)$	
Modified Parallel	$D_{bulk} = D_1\phi_1\beta_1 + D_2\phi_2\beta_2$	



Composite Conductivity Models
Single Conductive Phase

Second group: consider volume fractions and phase geometries

NAME	FORMULA	MICROSTRUCTURE
Modified Parallel	$\sigma_t = \sigma_o \phi_o \beta_o$	
Archie's	$\sigma_t = \sigma_o {\phi_o}^{m_o}$	Sedimentary Rocks
Maxwell	$\sigma_t = \sigma_o \left[\frac{(d-1)\phi_o}{d-\phi_o} \right]$	
DEM	$\sigma_t = \sigma_o {\phi_o}^{(d/(d-1))}$	
Self-Consistent (SC)	$\sigma_t = \sigma_o \left[\frac{d\phi_o - 1}{d-1} \right]$	

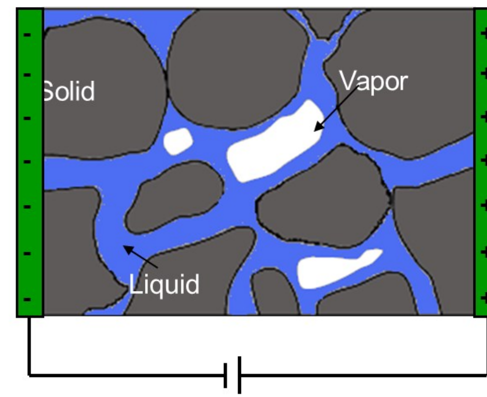
- d describes spatial dimension not phase geometries
- But, it has been used empirically to describe phase geometries

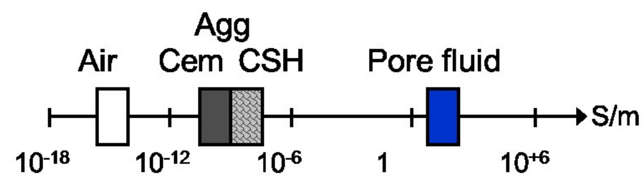
(McLachlan et al. 1990, Torquato 2002)

Parallel Law Modified

- Considers pore fluid as the only conductive phase
- Pore fluid (capillary, gel pores

$$\rho_{Bulk} = \rho_{Pore} \cdot \frac{1}{\phi\beta} = \rho_{Pore} \cdot F$$





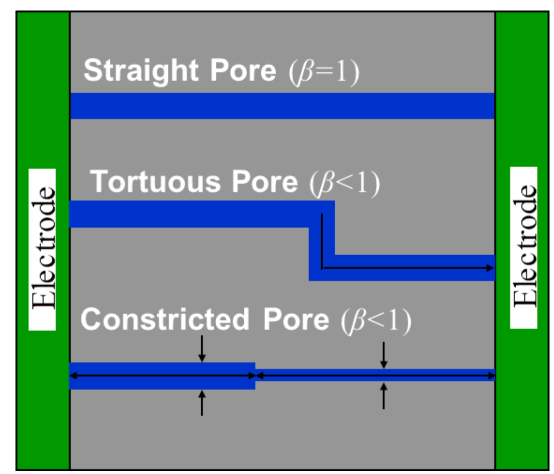
ρ_{Bulk}: concrete conductivity (S/m)

ρ_{Pore}: pore solution conductivity (S/m)

F: Formation Factor

ϕ: pore volume fraction

β: avg. liquid connectivity (describes liquid tortuosity and constrictedness)



(Garboczi 1990, Christensen et al. 1994, Rajabipour 2006)

Comparison of Different Manufacturers

σ, ρ

Geometry

3 Factors

Pore soln

Porosity

Tortuosity

Variability

Saturation

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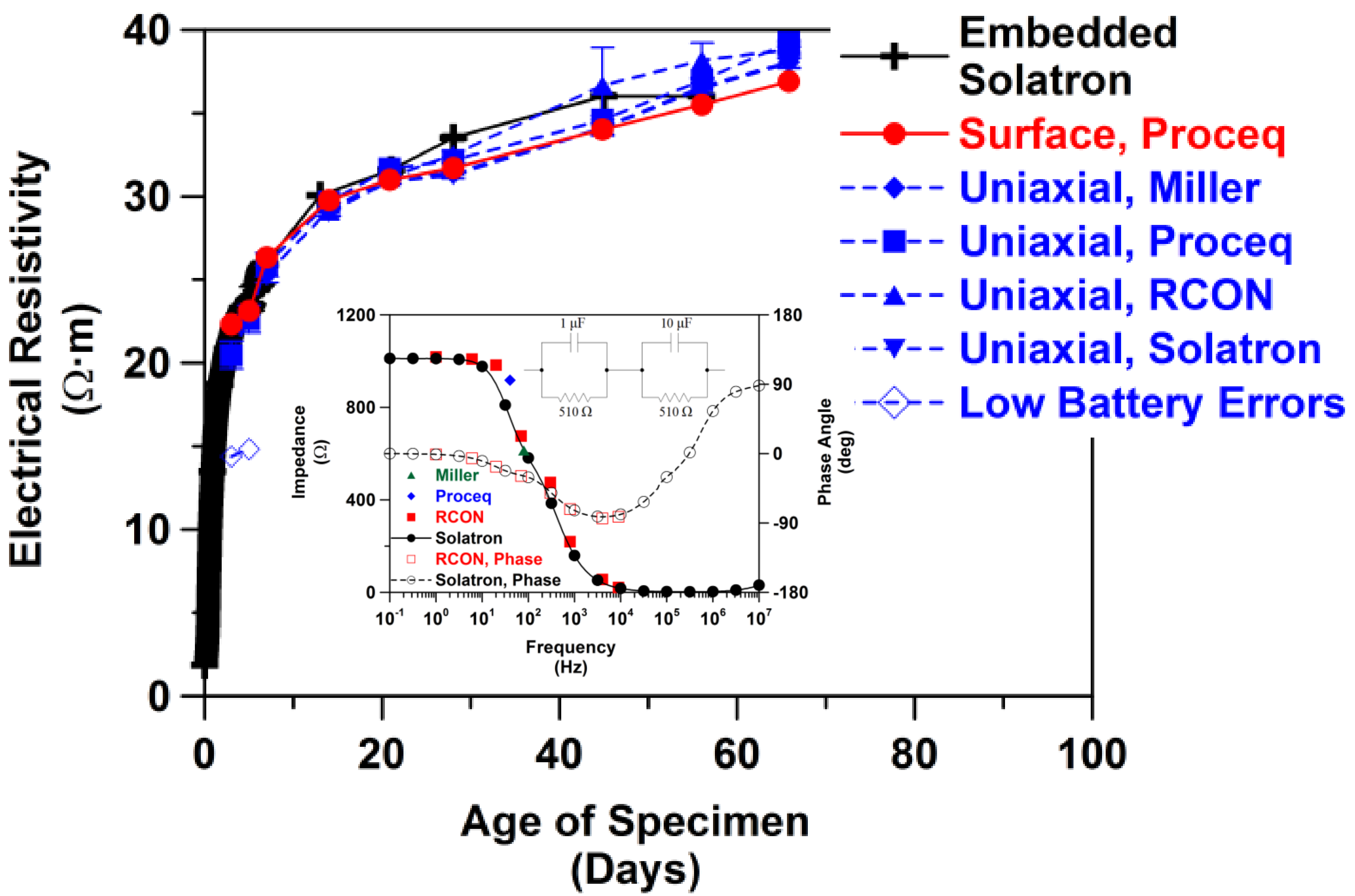
Field Use



Spragg et al. 2012

Lets Start with Notation and Archie

σ, ρ

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Field Use

- Using resistivity, while I prefer conductivity, tests in practice that have discussion in ρ

$$\rho = \frac{1}{\sigma}$$

- Assume the only conductive phase is the fluid and the resistivity of the concrete is the product of resistivity of solution and the formation factor (inverse porosity and connectivity) (solutions exist for other conductive phases Weiss et al.)

$$\rho = \rho_O \frac{1}{\phi} \frac{1}{\beta}$$

Relationship Between Q (Coloumbs) and Resistivity (ρ)

- σ, ρ
- Geometry
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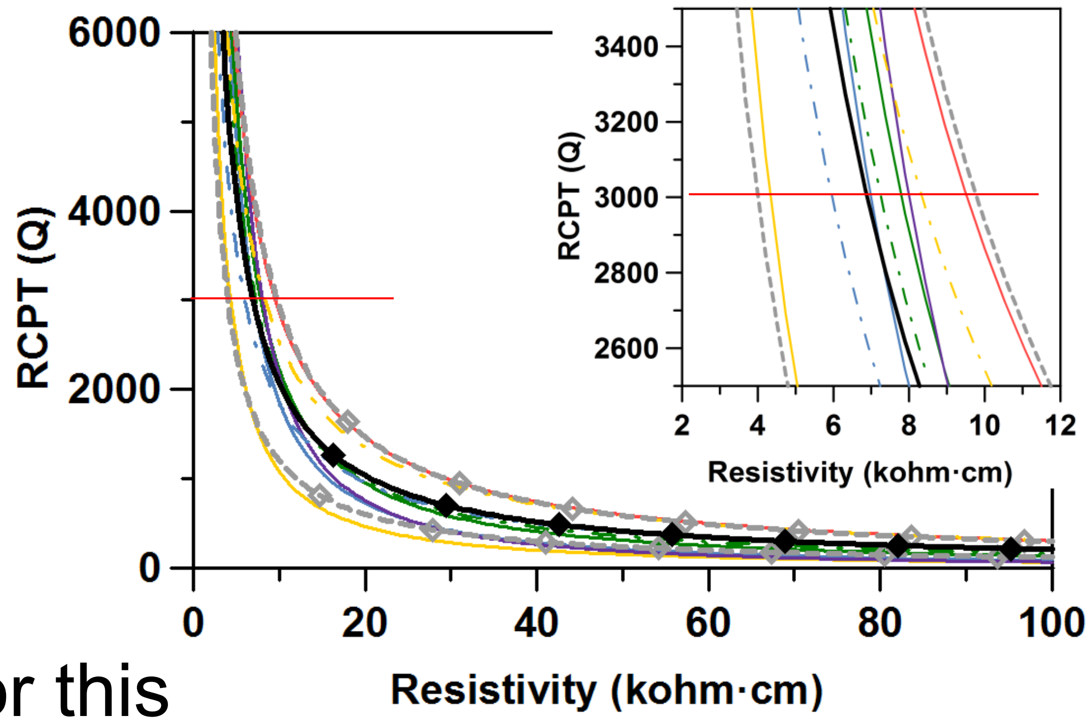
- Field Use

- Many relationships have been developed over the years (the black - theory) $Q = \int_{0h}^{6h} \frac{V}{\rho\kappa} dt$
- While all have a reasonable shape, details are very important when one tries to use this in spec's
- Explored reasons for this



Spragg et al. 2013

Components of Variation

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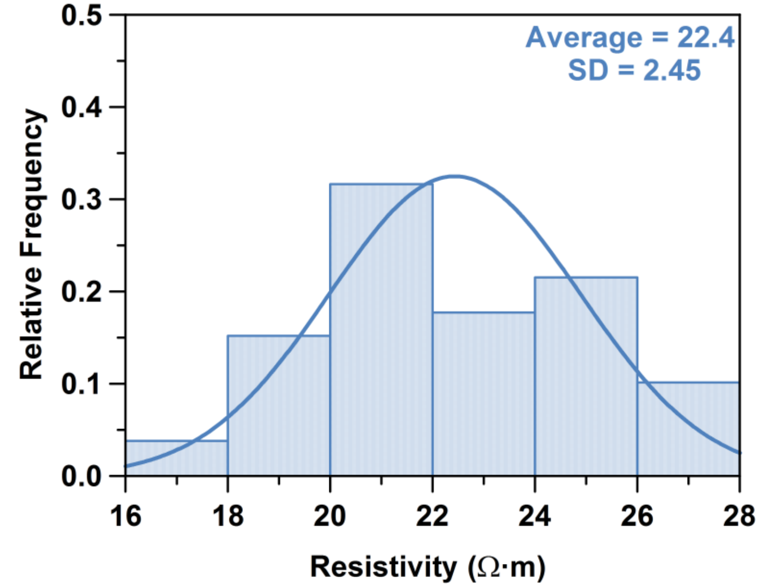
$$\sigma_{total} = \sqrt{\sigma^2_{machine} + \sigma^2_{operator} + \sigma^2_{material} + \sigma^2_{production} + \sigma^2_{curing}}$$

- Machine/Operator/Material
  - Traditionally estimated in a single lab as
  - 3-4% (Purdue, LaDOT)
- Production
  - Important when used as a QC/QA tool
  - Dependent on contractor quality
  - 10% is a typical value



- Data shown is from a central mix plant with one mixture run frequently, low variation

Spragg et al. 2012

Components of Variation
Attention to Curing is Critical

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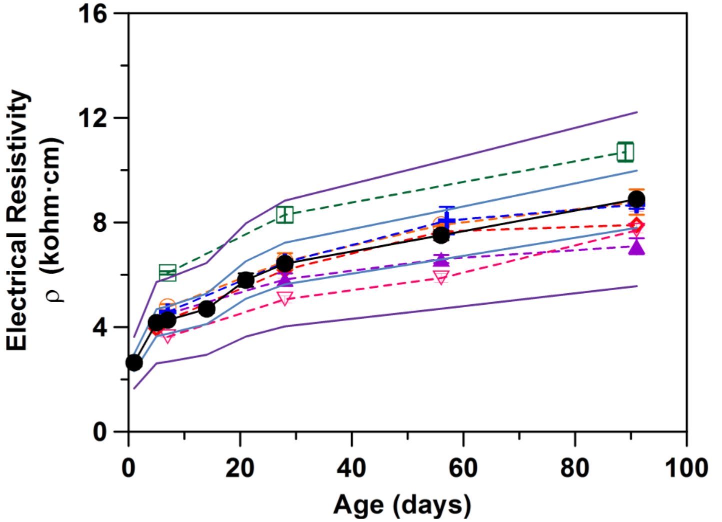
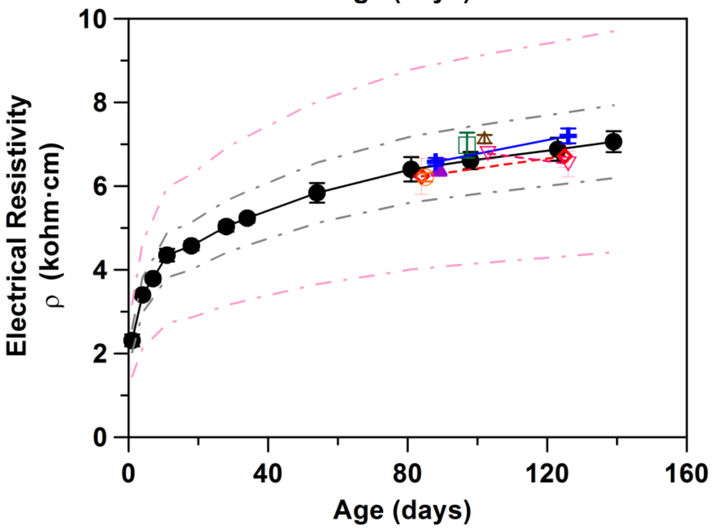
Field Use

- AASHTO RR (12)
- Within-lab: 4.36%
  - Machine/Operator/Material
- Multi-lab: 13.22%
  - Machine/Operator/Material and curing
  - Believed Curing Variation: 12.5%
- State Variation Shown (top young, bottom old samples)





Spragg et al. 2013

Incorporating Aspects of Curing

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- Spragg developed a program to investigate factors that could influence curing (not discussing temp or RH here that change DOH)

$$\rho = \rho_o^* \cdot F \cdot f(S) \cdot f(T_{Testing}) \cdot f(Leach)$$

- ρ is the resistivity at an equivalent age $t_{equivalent}$
- ρ_o^*: pore solution resistivity at saturation
- $f(S)$ saturation function
- $f(T_{testing})$ testing temperature correction
- $f(Leach)$ leaching function

Spragg et al. 2013

Degree of Saturation and Its Impact on Transport

σ, ρ

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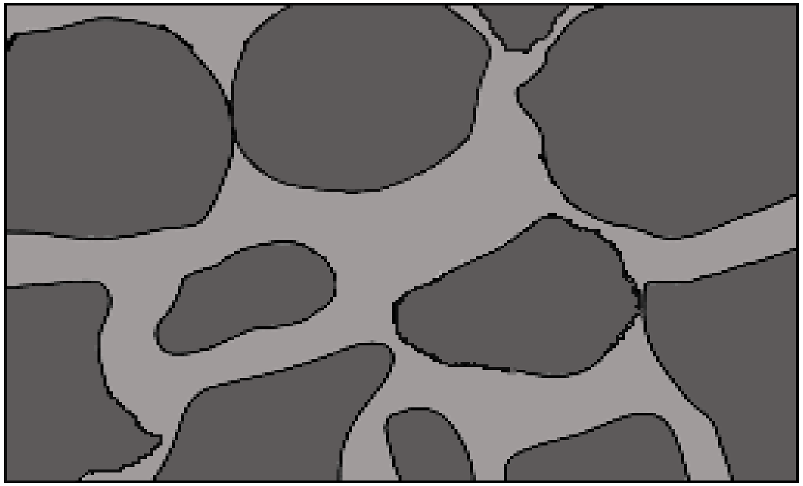
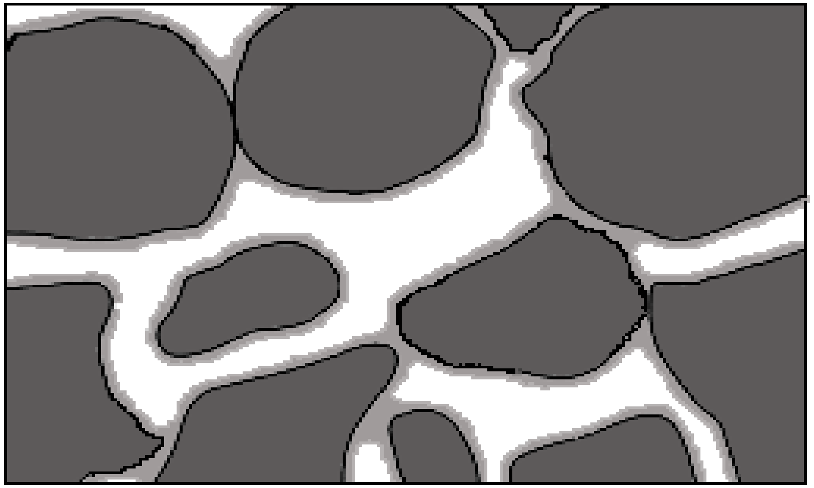
Field Use

- Transport in the fluid phase depends on the volume and connectivity of the fluid phase
- Transport in the vapor phase depends on the volume and connectivity of the vapor phase



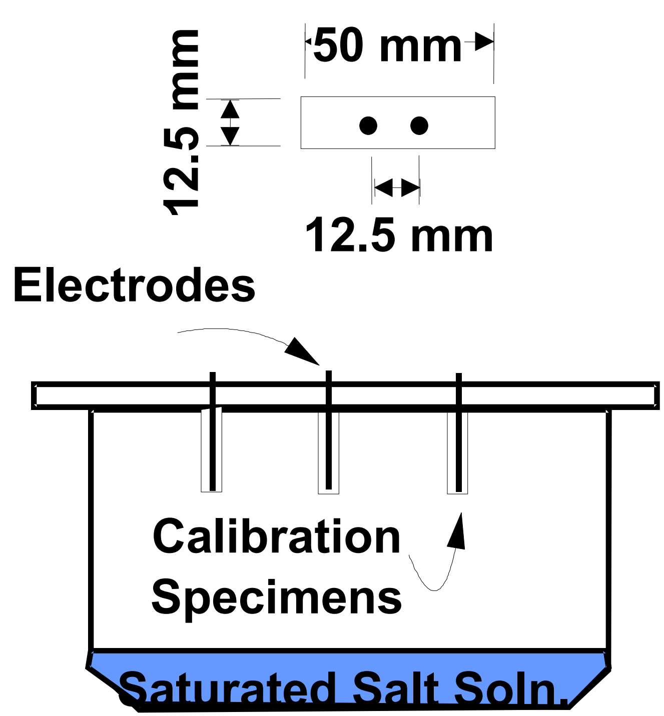
Saturated

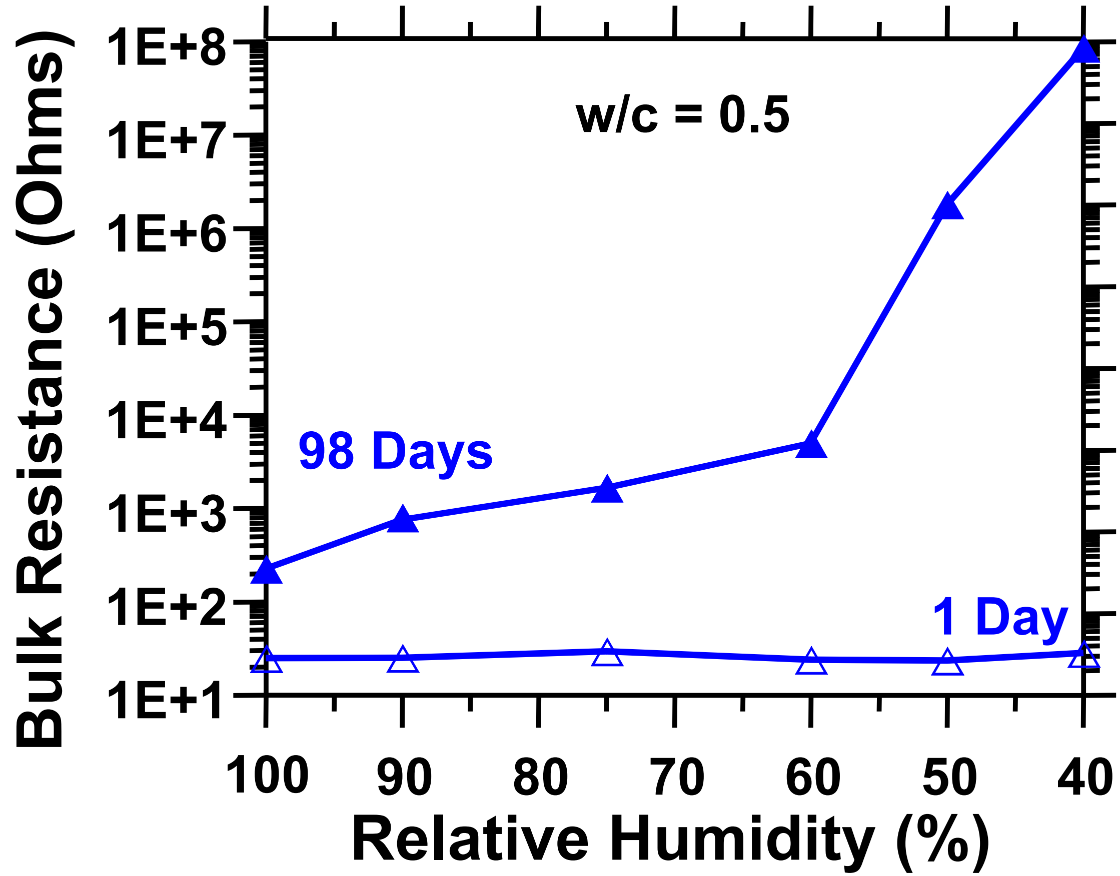


Drying

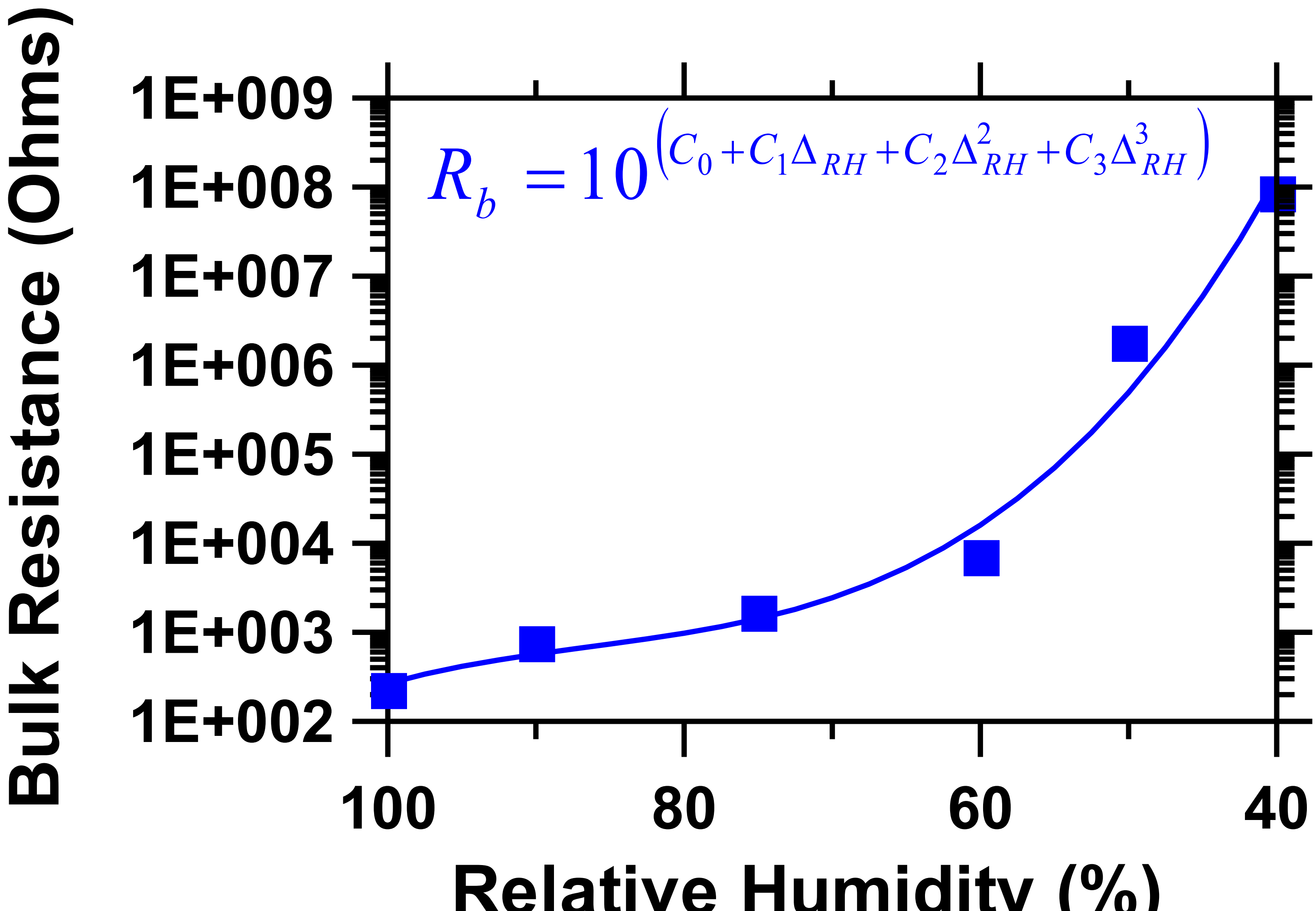
Drying of a High w/c Systems

Calibration Specimens

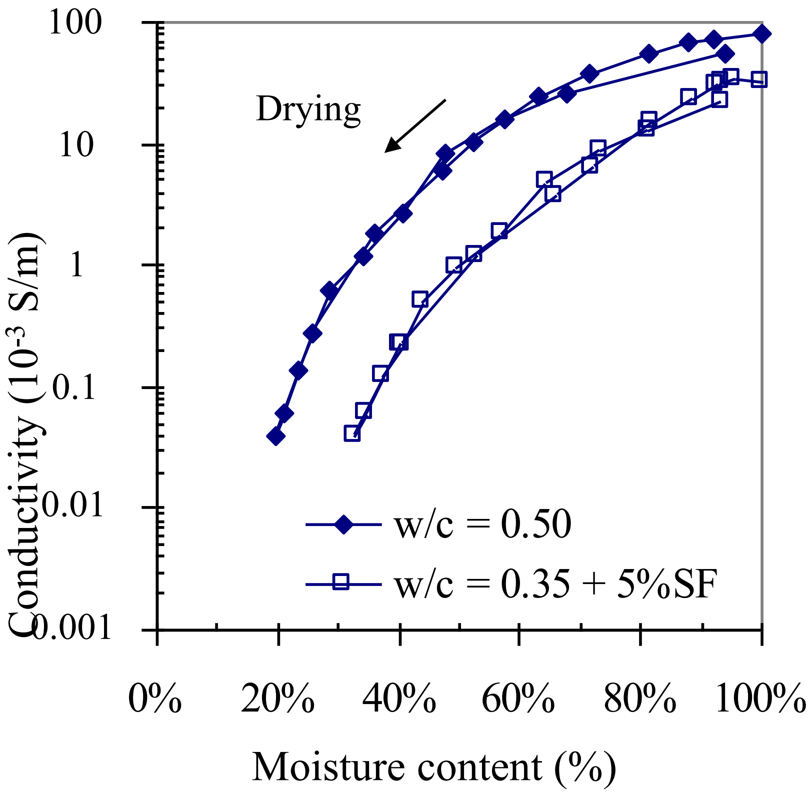




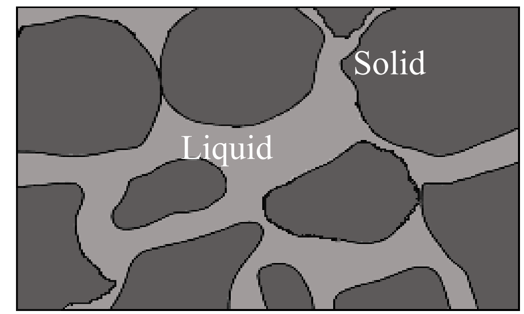
Correlating Bulk Resistance with Humidity - 98 Days



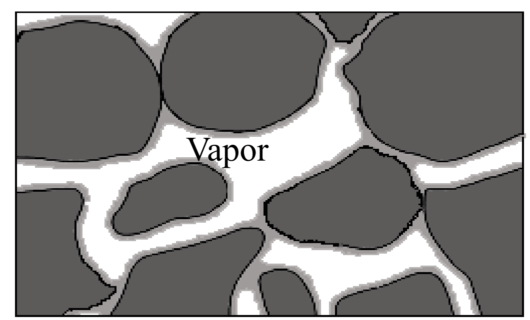
What Parameters Affect Conductivity?



Saturated



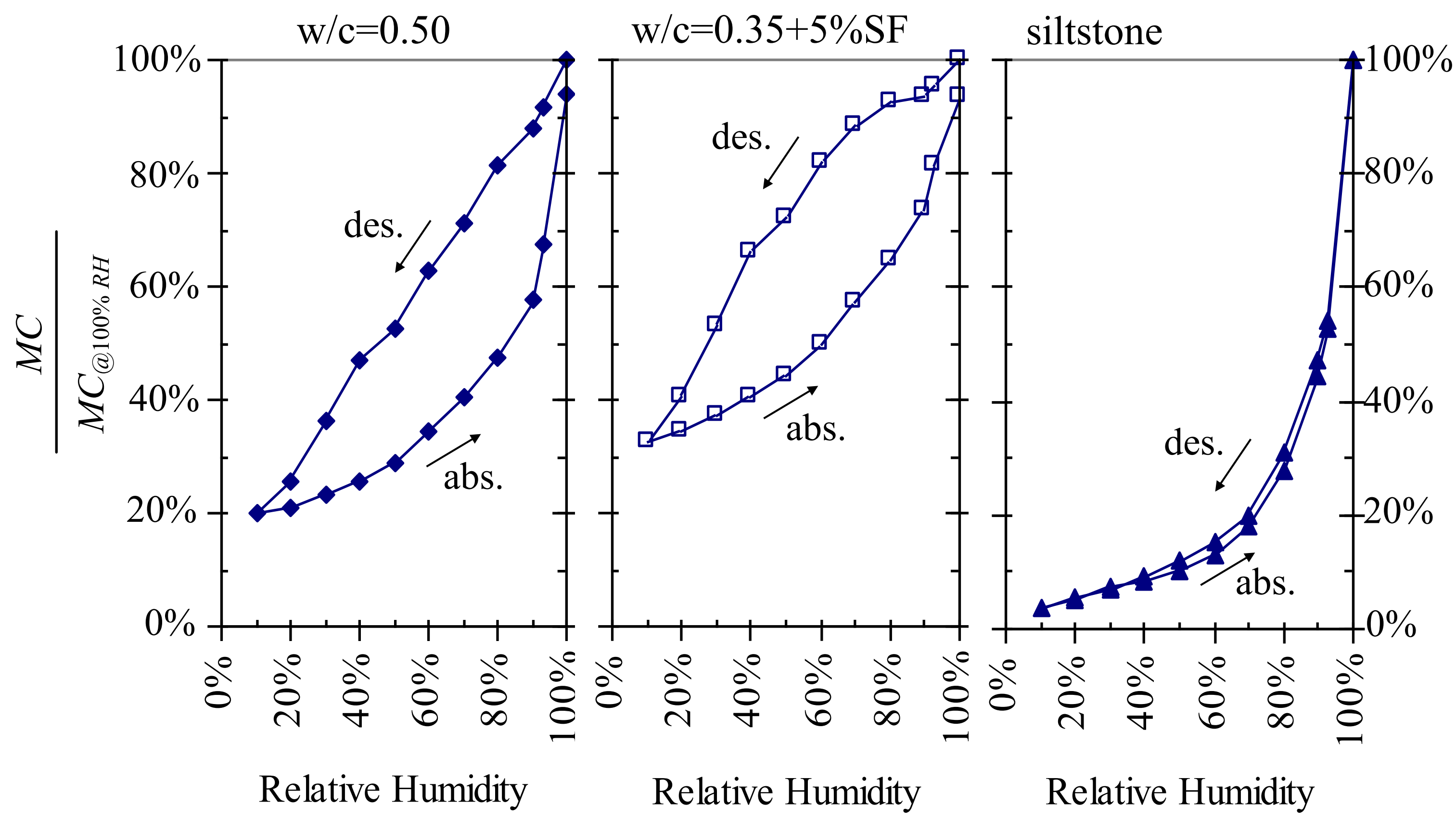
Drying



$$\sigma_t = \sigma_o \phi \beta$$

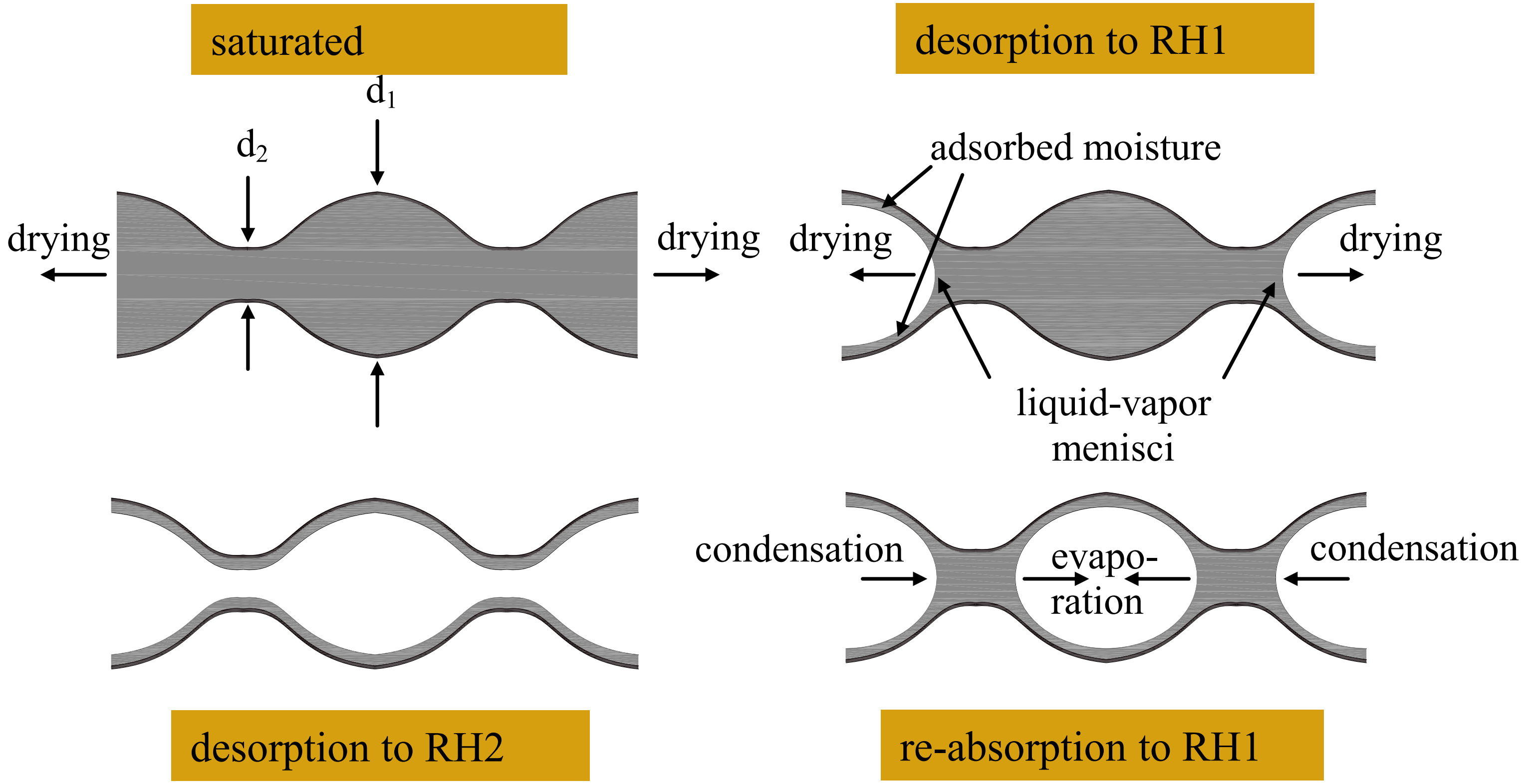
(Rajabipour and Weiss 2007)

Moisture Content Isotherms



Significant hysteresis in cement pastes

Desorption-Absorption Hysteresis

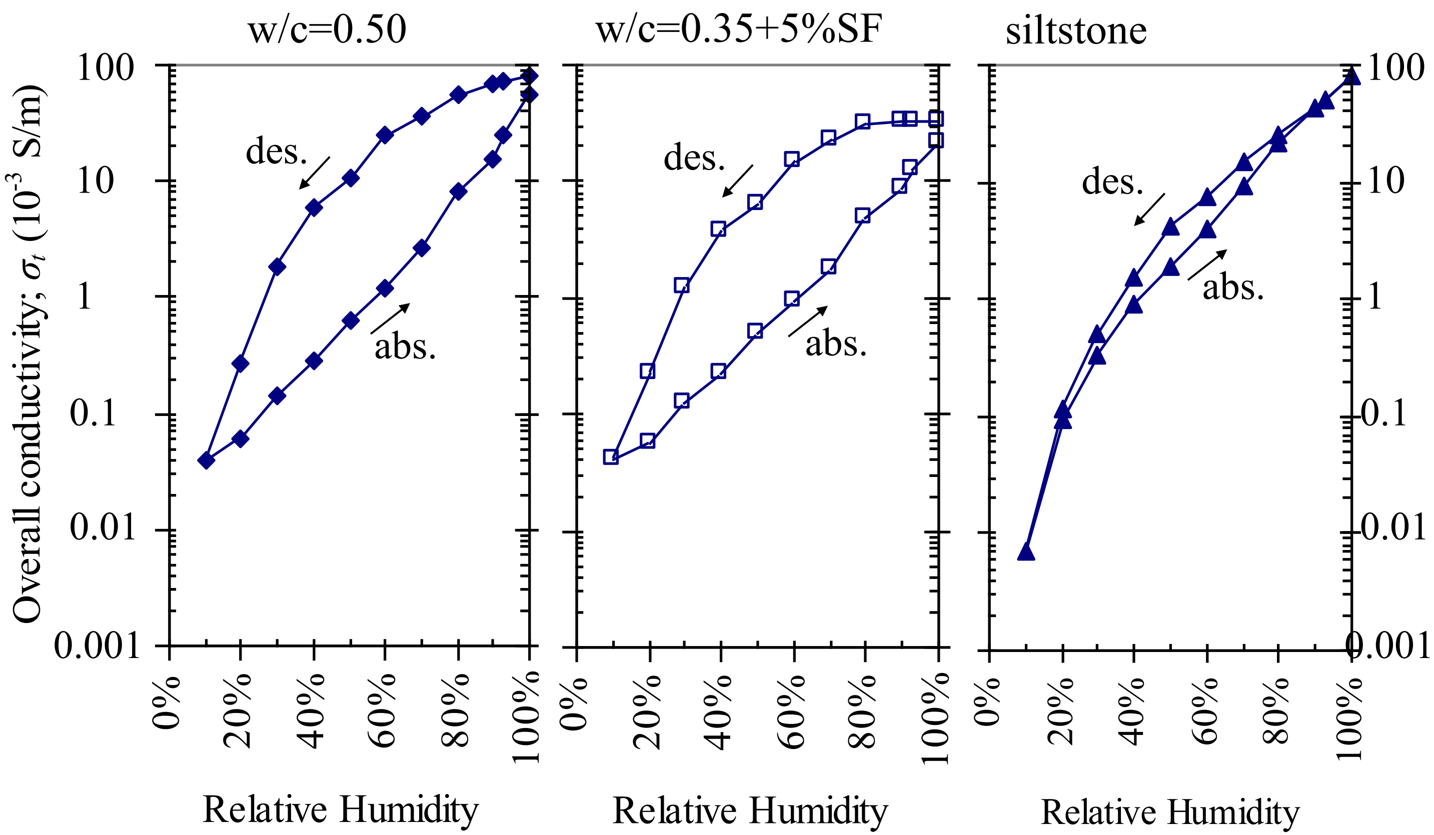


Feldman and Serada (1968):

1- Primary hysteresis at high to medium RH (>30%) due to pore constrictions

2- Secondary hysteresis at low RH (<30%) due to movement of interlayer water

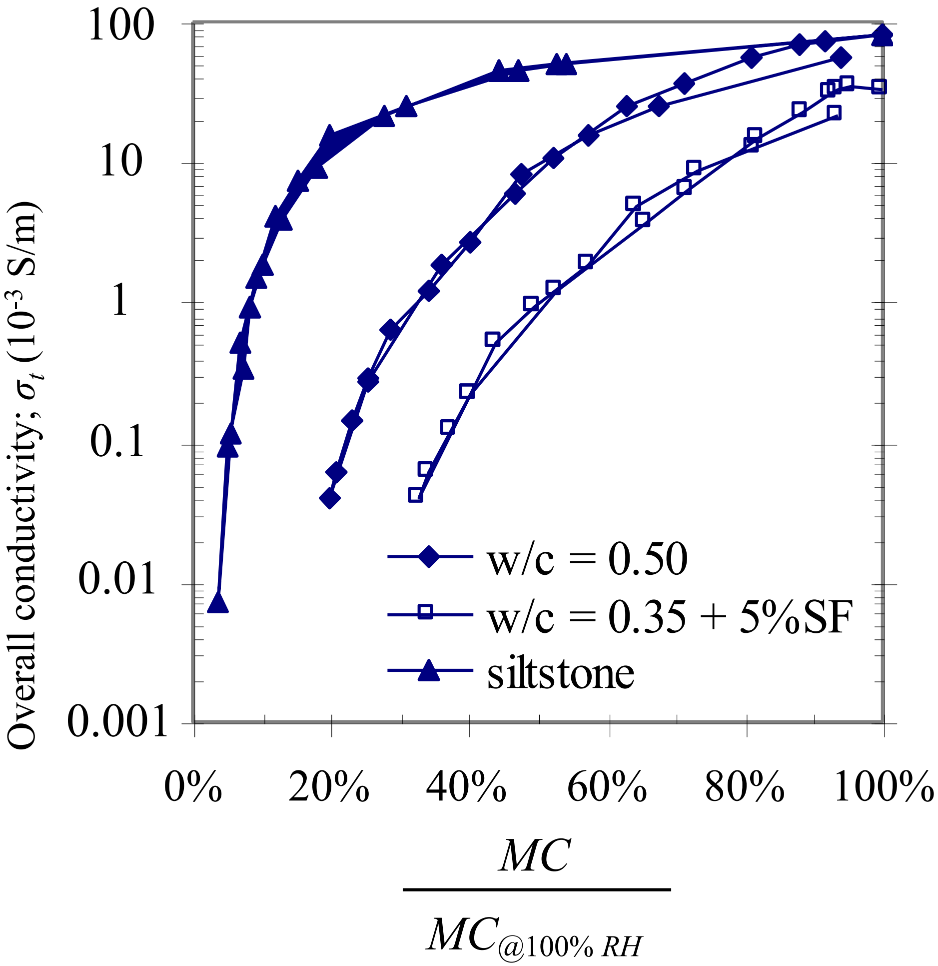
Electrical Conductivity Isotherms



- Significant hysteresis for cement pastes
- σ_t does not have a 1-to-1 correlation with RH (cement paste)
- estimation of RH based on σ_t can be erroneous (cement paste)

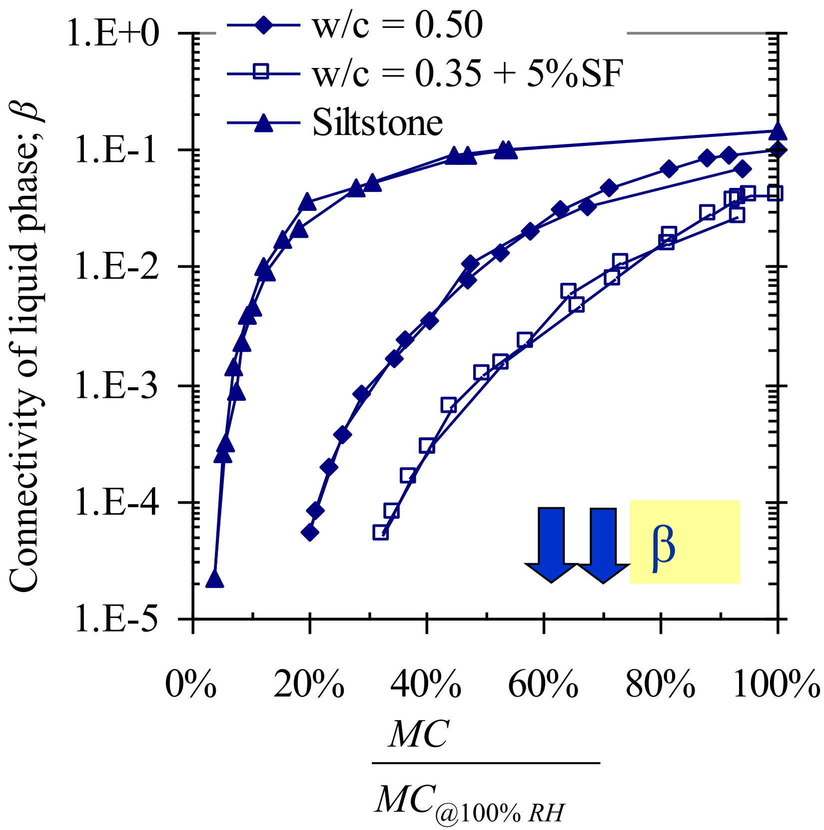
Electrical Conductivity Isotherms

- σ_t – MC: No hysteresis!!
- σ_t – MC: 1-to-1 correlation
- MC the parameter governing



Drying Cement Paste
How σ_t, σ_o, ϕ, and β change?

$$\sigma_t = \sigma_o \phi \beta$$



Moisture connectivity (β) is the most influenced:

- Conduction paths become longer and more tortuous
- Conduction thru adsorbed moisture
- Adsorbed moisture breaks (>25%RH), disconnection of many conduction paths
- Depercolation of liquid phase (conduction partially thru solid)

Alternative - Degree of Saturation

- Challenge:
  - Difficult to deal with the equation as each term will change

$$\frac{\sigma_t}{\sigma_o} = a\phi^m$$

  - Approach – describe the formation factor for a saturated system

$$\frac{\sigma_t}{\sigma_{o(s)}} = \frac{1}{F} f(S)$$

  - The formation factor is the ratio of the resistivity with two solutions (system with water/system with brine)

Degree of Saturation

- Challenge:
  - Difficult to deal with the equation as each term will change
  - Approach – describe the formation factor for a saturated system
  - Then apply a saturation function (S^n)

$$\frac{\sigma_t}{\sigma_o} = a\phi^m$$

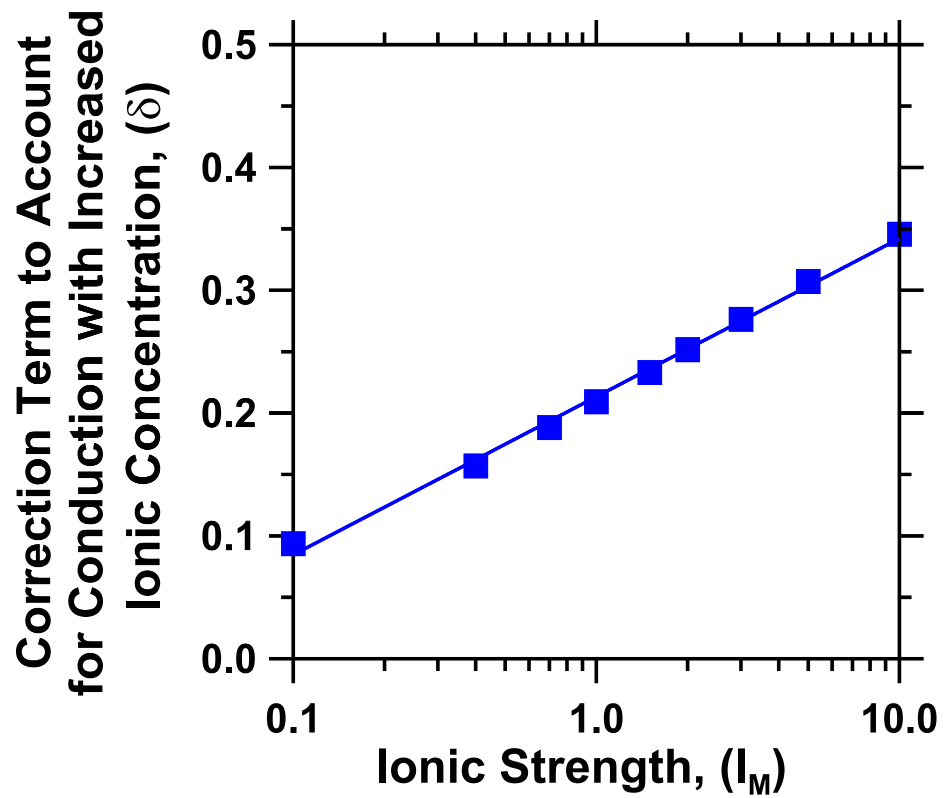
$$\frac{\sigma_t}{\sigma_{o(s)}} = \frac{1}{F} f(S)$$

$$\sigma_t = \left(\frac{\sigma_{o(S=1)}}{S}\right)\left(\frac{1}{F}\right) f(S)$$

Pore Solution Concentration

- Pore solution becomes more concentrated during drying

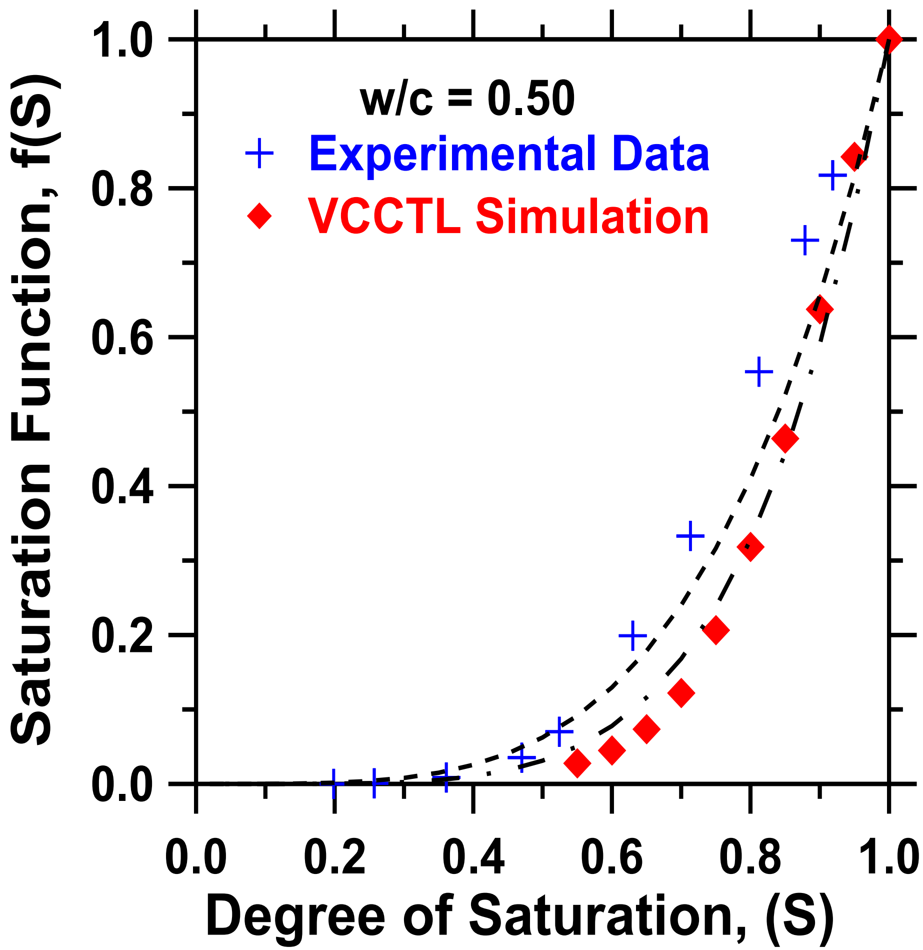
$$\frac{\sigma_o}{\sigma_{o(S=1)}} \cong \frac{1}{S}\left(\frac{1+G\sqrt{I_M}}{1+G\sqrt{\frac{1}{S}}\sqrt{I_M}}\right) = S^{\delta-1}$$



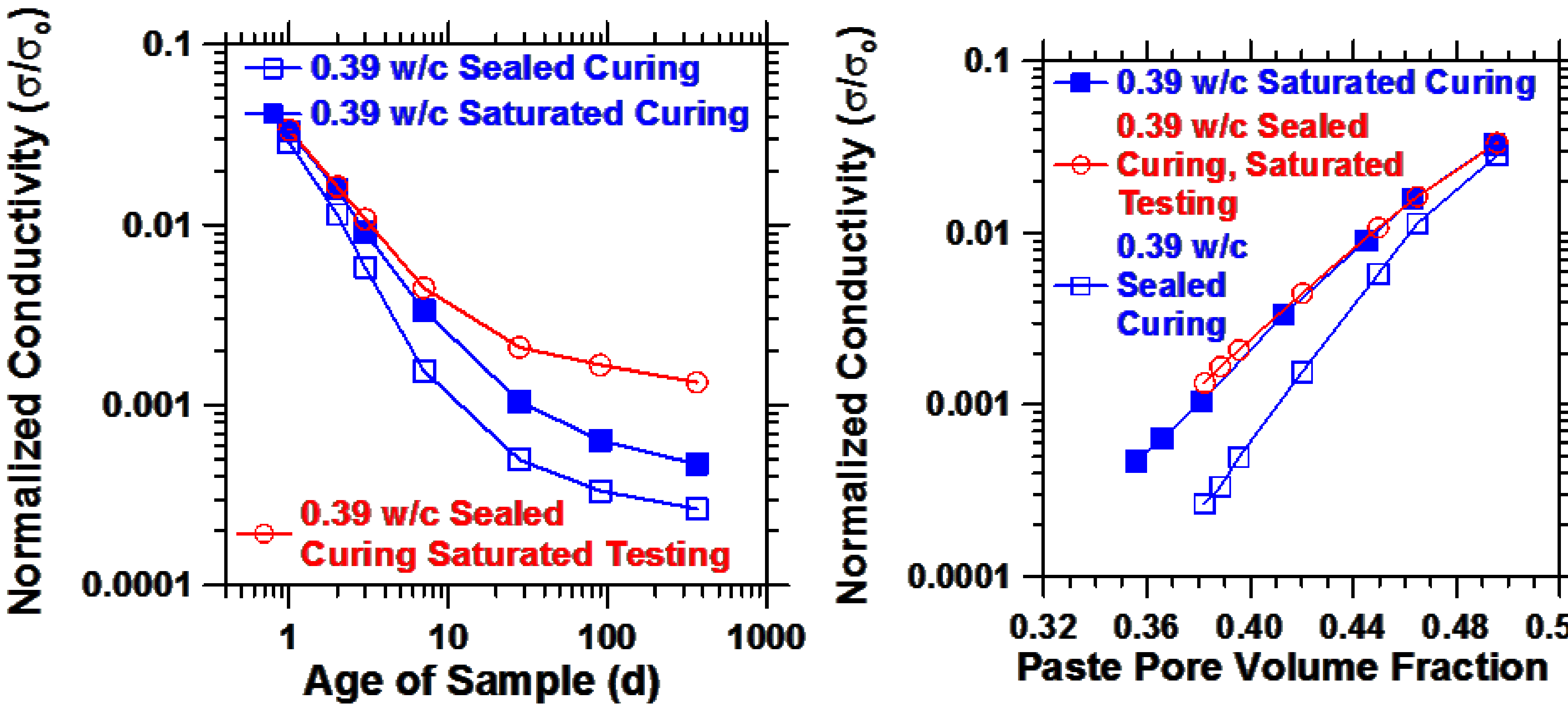
Degree of Saturation

- Instead of correcting each term independently it may be possible to treat all the terms with a single function

$$\frac{\sigma_t}{\sigma_{o(S=1)}} = \frac{1}{F} S^{n-1+\delta}$$



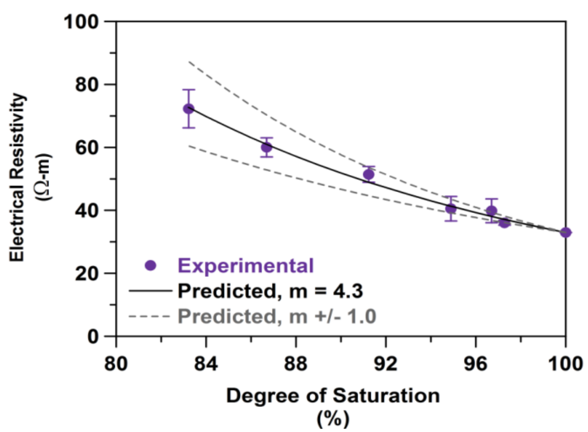
Curing/Saturation Conditions

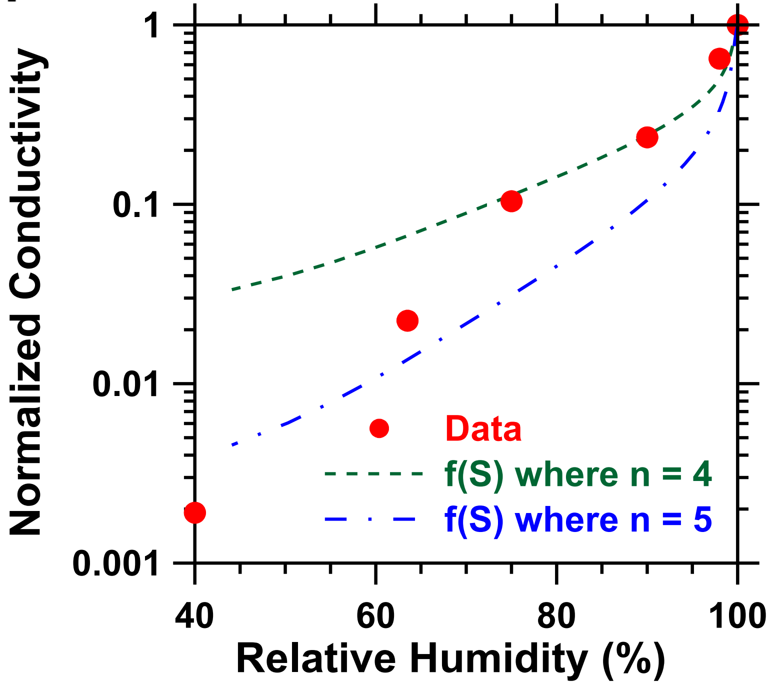


Saturation

σ, ρ
Geometry
3 Factors
Pore soln
Porosity
Tortuosity
Variability
Saturation
Temperature
Leaching
Acceleration
Field Use

- Weiss et al. (2012) approach accounted for loss of fluid, concentration of ions, and change in path, expression combines these
- $f(S) = S^m$
  - $m \approx 3 - 5$





Weiss et al. 2013

$$\rho = \rho_o^* \cdot F \cdot f(S) \cdot f(T_{Testing}) \cdot f(Leach) \text{ at } t_{equivalent}$$

Incorporating Aspects of Curing

σ, ρ
Geometry
3 Factors
Pore soln
Porosity
Tortuosity
Variability
Saturation
Temperature
Leaching
Acceleration
Field Use

- Spragg developed a program to investigate factors that could influence curing (not discussing temp or RH here that change DOH)

$$\rho = \rho_o^* \cdot F \cdot f(S) \cdot f\left(T_{Testing}\right) \cdot f(Leach)$$

- ρ is the resistivity at an equivalent age $t_{equivalent}$
- ρ_o^*: pore solution resistivity at saturation
- $f(S)$ saturation function
- $f(T_{testing})$ testing temperature correction
- $f(Leach)$ leaching function

Spragg et al. 2013

Maturity and Electrical Conductivity

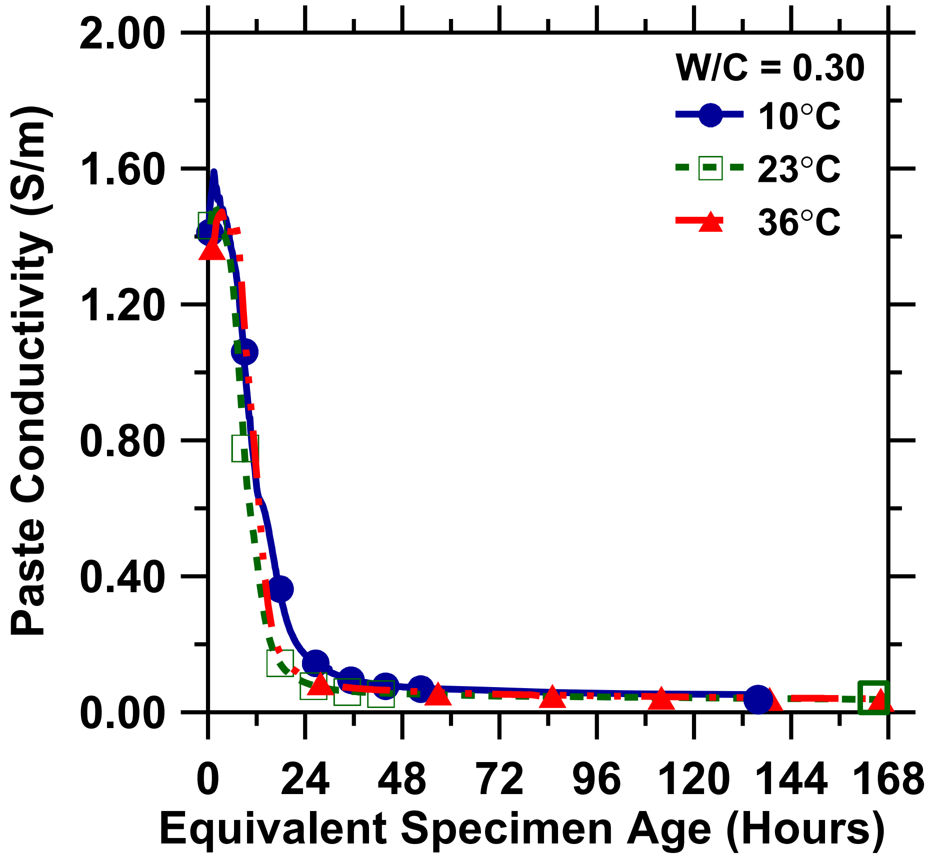
- Conductivity is a function of Maturity (hydration) and Temperature (conductivity)

$$\sigma(t) = f(M) \cdot f(T)$$

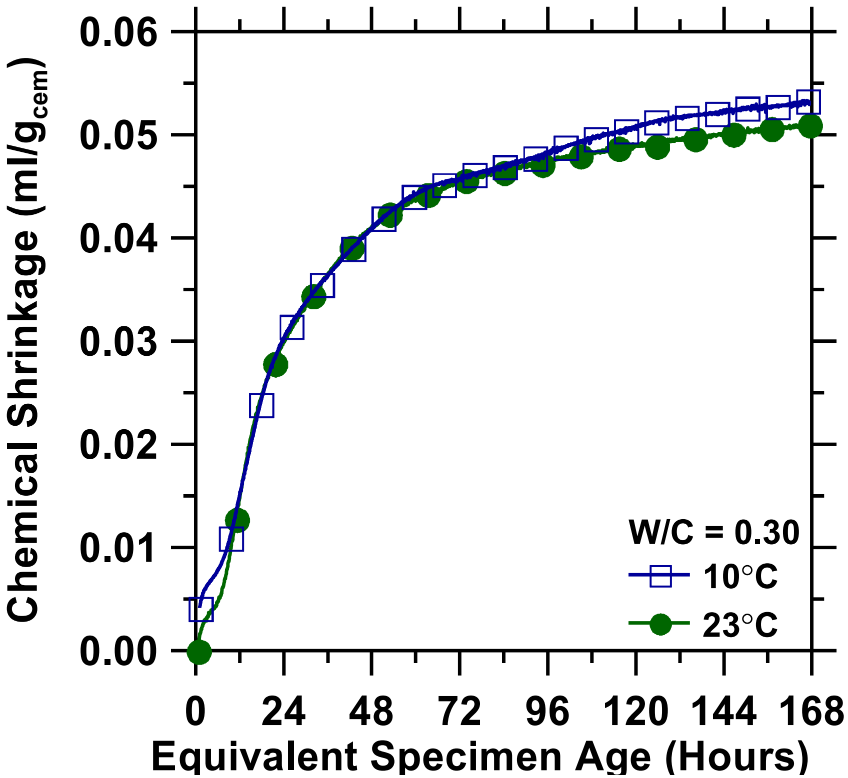
$$f(M) = \int_0^t \exp\left[\frac{E_{aR}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{REF}}\right)\right] \cdot dt$$

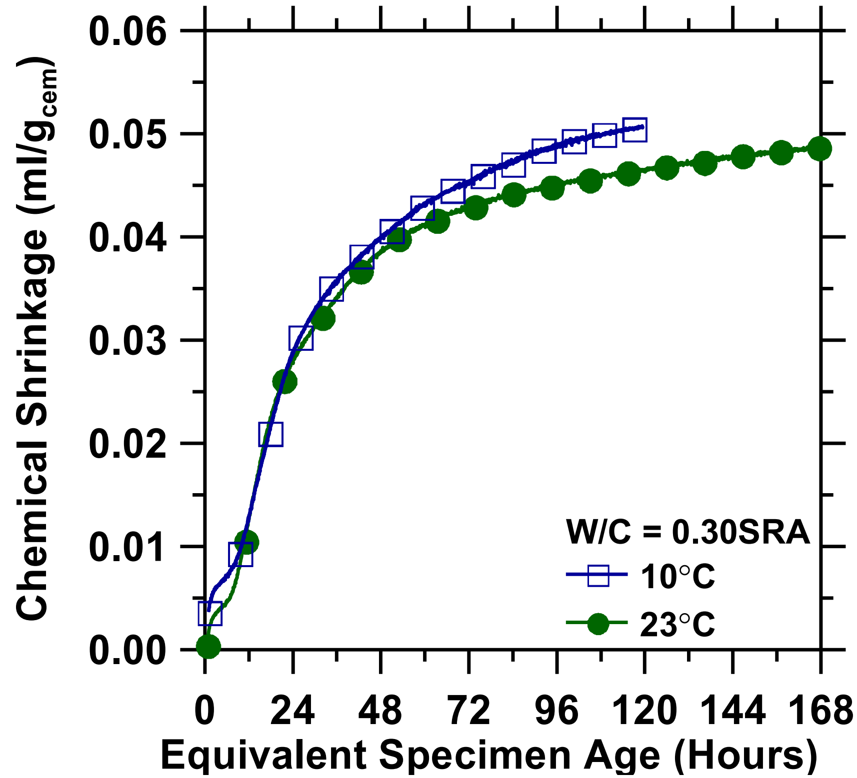
E_{aR} = 39.50 KJ/mole

$$f(T) = \frac{\sigma(T)}{\exp\left(-\frac{E_{aC}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{REF.}}\right)\right)}$$



Applicability of a Maturity Transformation to Cement Hydration





- Concept is applicable
- EAR = 37.5 KJ/mol
- Minor variations related absorption

$$t_e = \int_0^t \exp\left[\frac{E_{aR}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{REF}}\right)\right] \cdot dt$$

Testing Temperature

σ, ρ

Geometry

3 Factors

Pore soln

Porosity

Tortuosity

Variability

Saturation

Temperature

Leaching

Acceleration

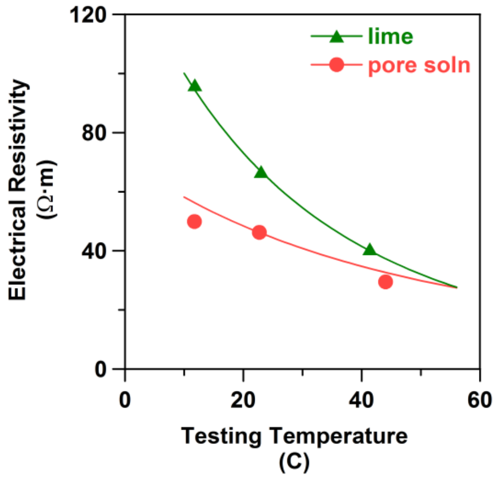
Field Use

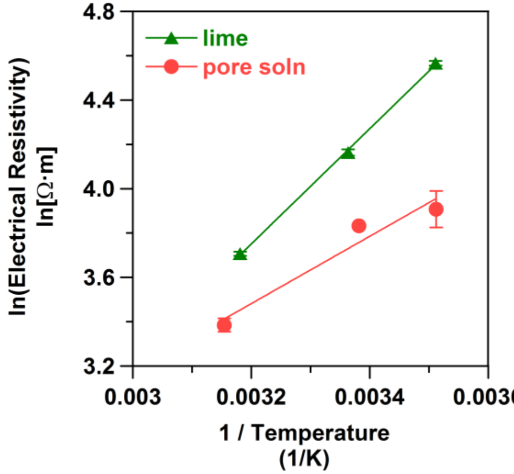
- Activation Energy of Conduction (test temp)

  Rajabipour et al. 2007, Sant et al.2007

$$\frac{\rho_{T_{ref}}}{\rho} = exp\left[\frac{E_{a-con}}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right]$$

- In the past we noticed differences between
- Varied the solutions
  - Pore Solution: 9-12 kJ/mol
  - Bulk Sample: 20-25 kJ/mol



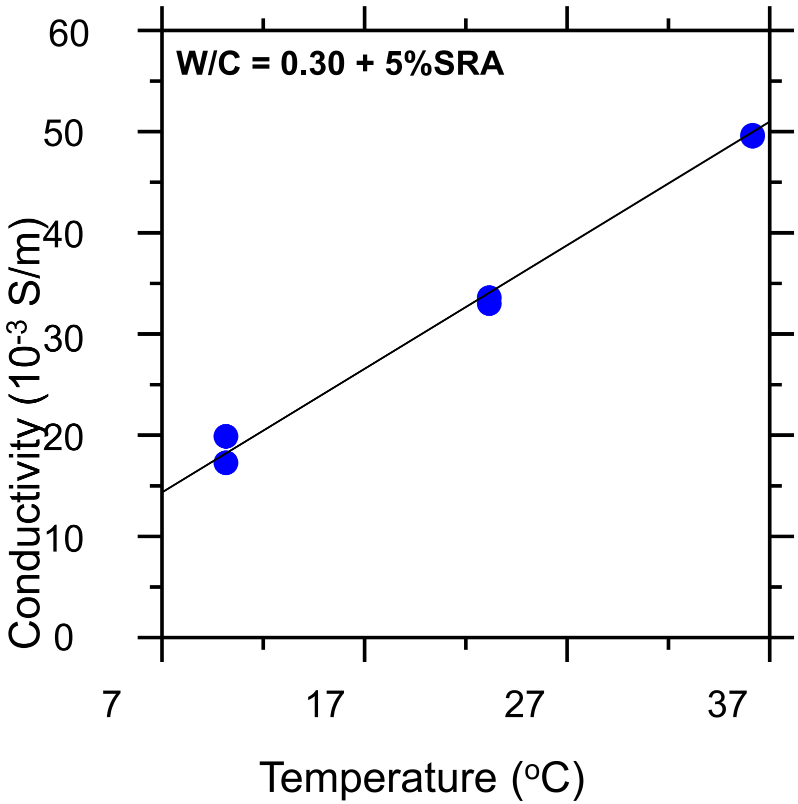


Spragg et al. 2013

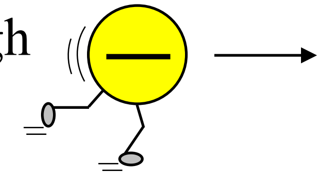
$$\rho = \rho_o^* \cdot F \cdot f(S) \cdot f(T_{Testing}) \cdot f(Leach)\ at\ t_{equivalent}$$

Arrhenius Law

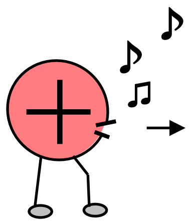
w/c	Eac (KJ/mole)
0.36	9.39
0.42	10.19
0.45	10.06
0.50	9.69
STD DEV	0.365



- High Temperature: High mobility, fast ions High conductivity



- Low Temperature: Low mobility, slow ions Low conductivity



$$\sigma(T) = Ae^{\left(\frac{-E_a}{RT}\right)}$$

- Higher temperature → higher conductivity

(Rajabipour 2006, Sant et al. 2008)

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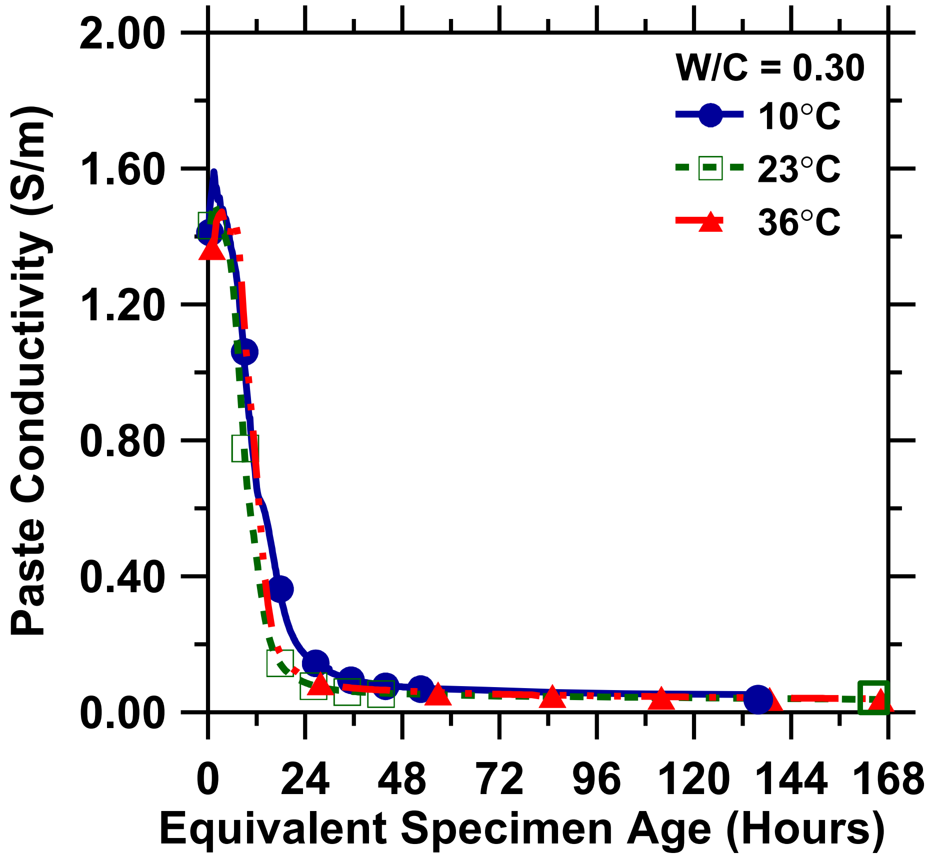

Incorporating Aspects of Curing

σ, ρ

Geometry

3 Factors

Pore soln

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Field Use

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- $f(S)$ saturation function
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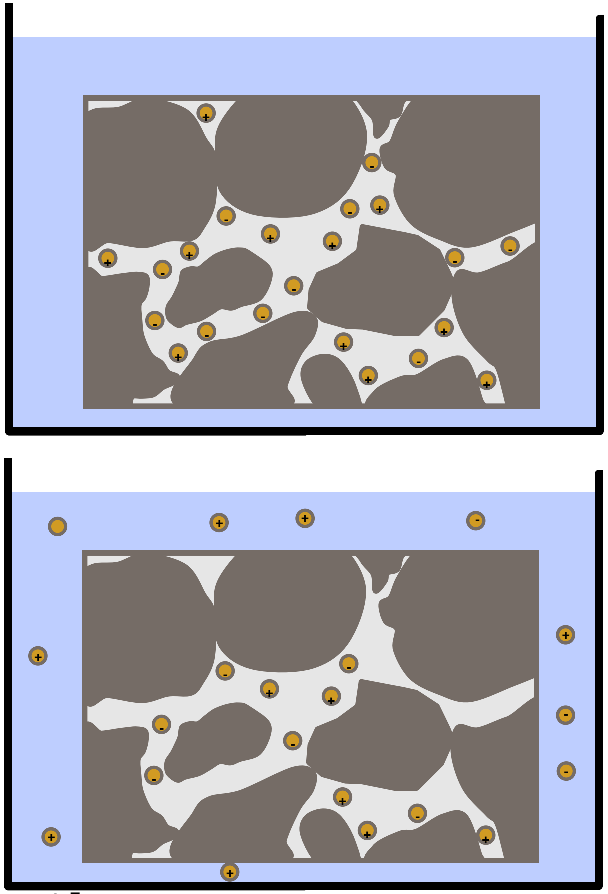
Spragg et al. 2013

Leaching During Storage

σ, ρ
Geometry
3 Factors
Pore soln
Porosity
Tortuosity
Variability
Saturation
Temperature
Leaching
Acceleration
Field Use

- Many people think of CH leaching
- However we are worried about alkali leaching
- Cement pore solution
  - OH^-, K^+, Na^+
  - $\rho \approx 40\text{–}100$ m ohm·m
- Standard Solution
  - $CaOH_2$ (CH)
  - $\rho \approx 1000$ milli ohm·m
- Measured storage solution

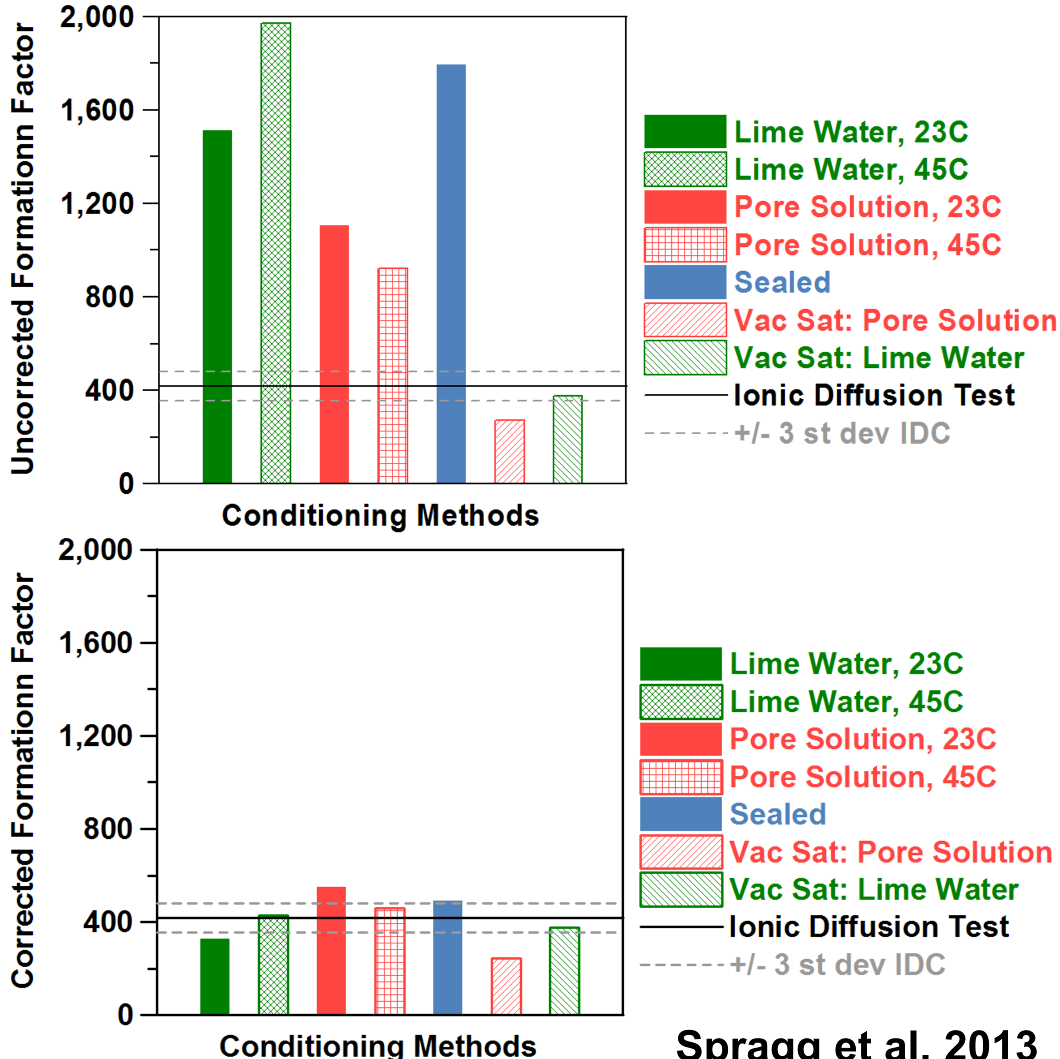


Spragg et al. 2013

Importance of Accounting for Several Factors

σ, ρ
Geometry
3 Factors
Pore soln
Porosity
Tortuosity
Variability
Saturation
Temperature
Leaching
Acceleration
Field Use

- Formation Factor – 420
- Top figure shows direct measurement
- Bottom has corrections applied for temperature, ionic strength, saturation, and leaching

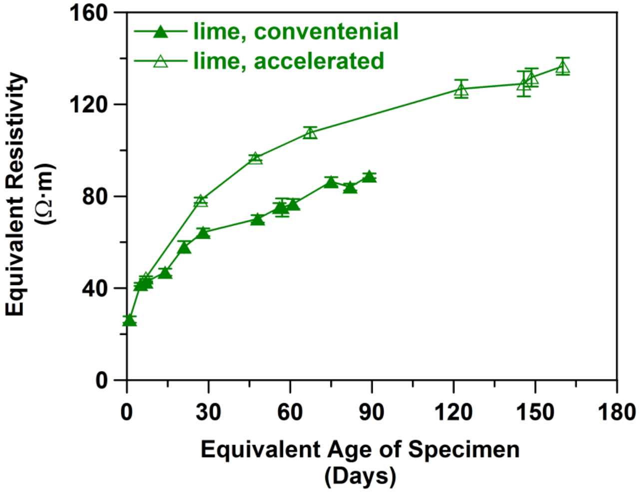


Spragg et al. 2013

Accelerating Curing Time

σ, ρ
Geometry
3 Factors
Pore soln
Porosity
Tortuosity
Variability
Saturation
Temperature
Leaching
Acceleration
Field Use

- Many materials we test take a long time to show benefits (91 d)
- We frequently want to speed this time up
- VTRC/NRMCA method
- Lime water 7d, 23C followed by 21d, 38C
- T equivalent 56d
- Application on the right shows difference ~25%



Bu et al. 2014

Accelerated Curing Effects

σ, ρ
Geometry
3 Factors
Pore soln
Porosity
Tortuosity
Variability
Saturation
Temperature
Leaching
Acceleration
Field Use

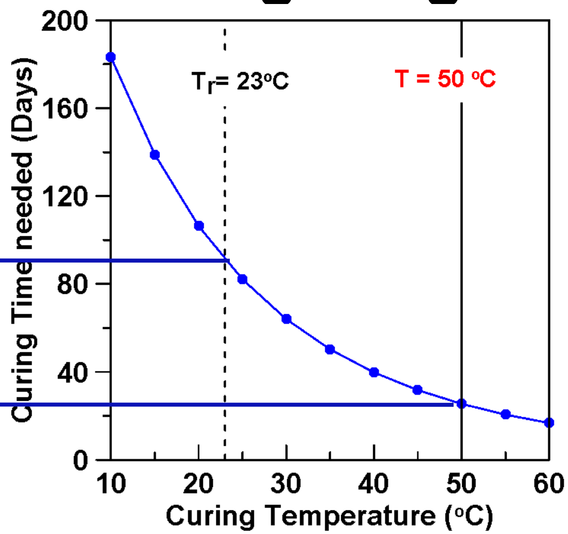
Transport testing and service life prediction usually performed on specimens of later age (91 days).

$$t_e = e^{-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)} t$$

Same maturity (DOH) could be achieved with shorter time using a higher curing temperature.

91 days

23 days



E_a = 37 kJ/mol

Bu et al. 2014

Role of Fluid Expansion

σ, ρ
Geometry
3 Factors
Pore soln
Porosity
Tortuosity
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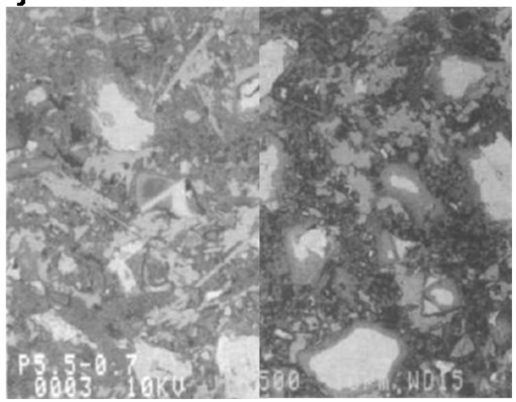
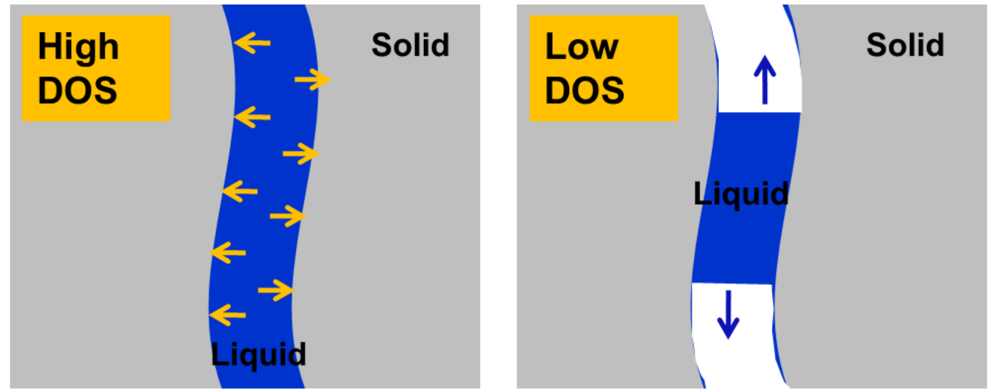
Saturation
Temperature
Leaching
Acceleration
Field Use

Kjellson et al. 1990





- Examined normal and accelerated curing with samples at different temperatures that were sealed/saturated

	Porosity (%)	D_{Cl^-} (10^{-11} m²/s)
NA-Wet	16.4	3.66
AA- Sealed	16.3	3.71
AA- Wet	17.5	4.81

Saturated Samples 24%

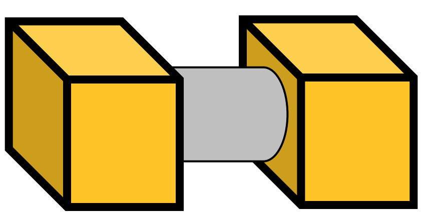
Bu et al. 2014

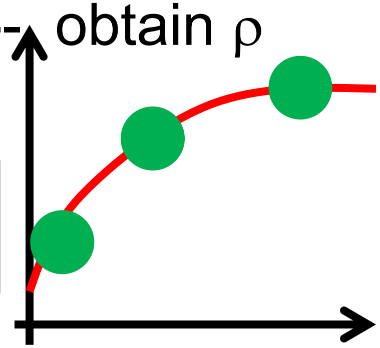
Applications – Acceptance Phase

- σ, ρ
- Geometry
- 3 Factors
- Pore soln
- Porosity
- Tortuosity
- Variability
- Saturation
- Temperature
- Leaching
- Acceleration
- Field Use

Mixture Acceptance

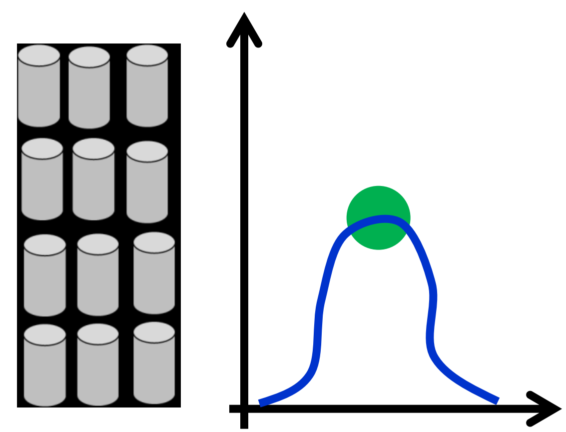
- Before construction to "qualify mixture"
- Time to corrosion
  - Absolute value of D
- Development of master curve data
  - strength v time
  - resistivity v time
- Specify F ---- obtain ρ





Quality Control

- Measurements during construction
- Test with good repeatability
- Easy tests allow for large sample size, statistical information as well



Summary and Recommendations

σ, ρ
Geometry
3 Factors
Pore soln
Porosity
Tortuosity
Variability
Saturation
Temperature
Leaching
Acceleration
Field Use

- Electrical properties
  - resistivity is a material property (geometry)
  - F is a material property (defined saturated)
  - test temperature important
  - degree of saturation
  - ionic leaching
  - curing can have major impact on variability
- Accelerated Curing
  - Maturity Method Can Be Applied
  - Accelerated Aging Causes Differences – Suggest Sealed Samples (low Pressure)