

# Measuring Transport Properties in Concrete: Lessons Learned and Implications

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# Thanks to Those Involved



- PI: Tommy Nantung
- Purdue: Castro, Poursae, Castro, Qian, Bu, Spragg, Villani, Olek, undergrads, Weiss
- NRMCA – Obla, Kim, Lobo
- States – FHWA, CO, IA, IL, IN, KS, MI, MN, MO, NY, PA, WI
- I – Review Tests
- II – Evaluate, III - Modify Tests
- IV – Correlate Test with Performance
- V – Performance Criteria, VI - Training

# Lets Think a Bit About Beams

**Need for a New Approach**

Transport Mechanisms

Pore Structure & Degree of Sat.

Gas Transport (Perm & Diff.)

Diffusion Using Fick's Second Law

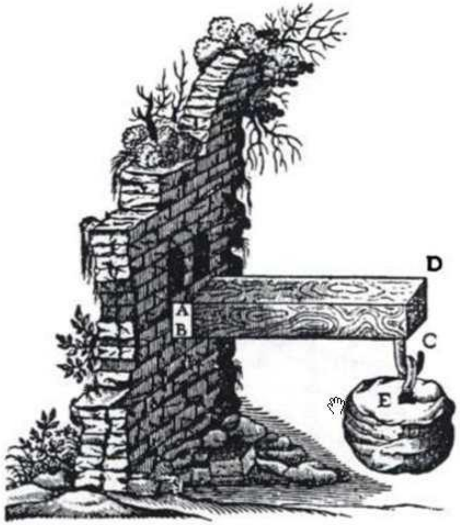
Electrical Props Factors of Interest

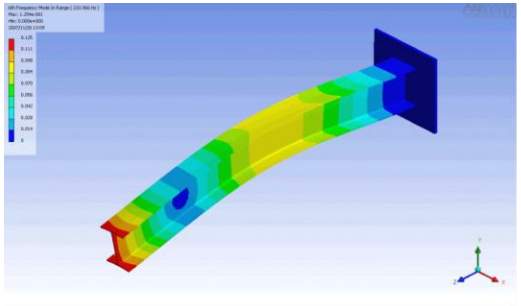
Accelerated Curing

Absorption

Summary & Recommendation

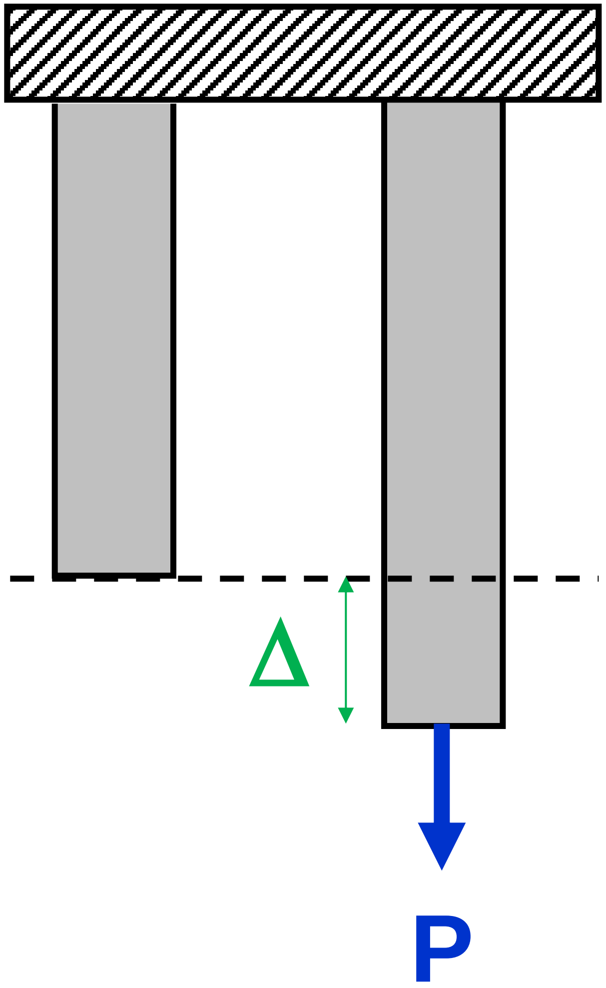
- Galileo in 1638 began "Dialogues on two new sciences"
- Parent later (1713) got strain and stress correct but ignored
- Euler and Bernoulli (1750) put together useful theory but there was a distrust that academia could be trusted for practical applications
- Bridges and buildings designed by precedent until the late 19$^{th}$ century
- Students are taught that 'models'/'equations' exist to describe structural response to load stimuli



# Today We Have A Stimulus, Response, and Material Property






**Material Property (E)**

**Stimulus –**
**Application of a Force (P)**

**Response –**
**Deformation (Δ)**

$$\Delta = \frac{PL}{AE}$$

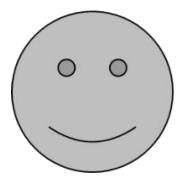
$$\sigma = \boxed{E} \cdot \varepsilon$$

# Some Quick Thoughts



- Statics, dynamics, strength of materials on nearly every campus give students
  - models or equations
  - boundary conditions and
  - material parameters
- We generally approach durability in a very different way





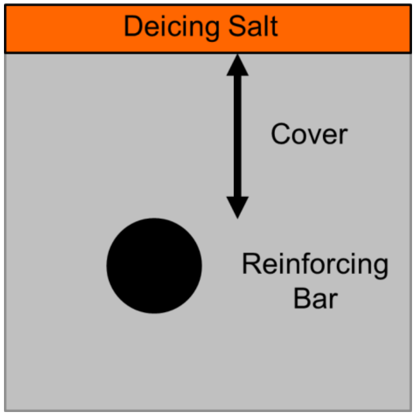

- We can improve with a scientific approach
- Time is ripe for our profession to tackle this

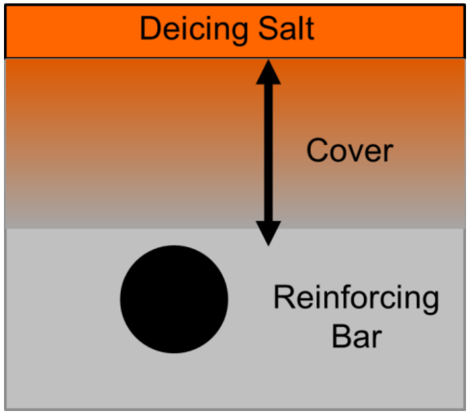
# Can We Write 'Durability' Equations

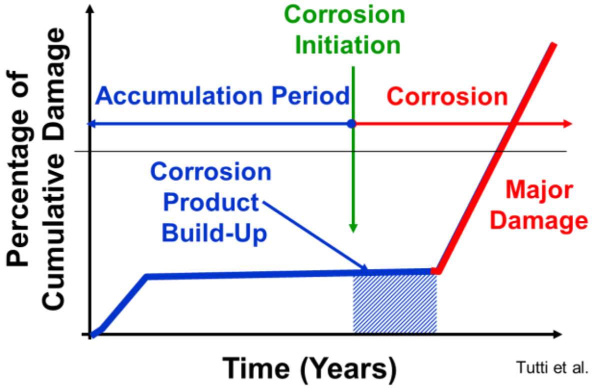


- 1970's deicing salts become widely used for clear pavements
- US: 8-12 mil. annual tons of salt
- Ions travels through concrete, depassivates steel, & corrodes
- Can we write an equation to predict when chloride reaches a critical level at the bar?


Photo Credit Dolch



# Fick's Second Law For Diffusion

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Diffusion Using Fick's Second Law

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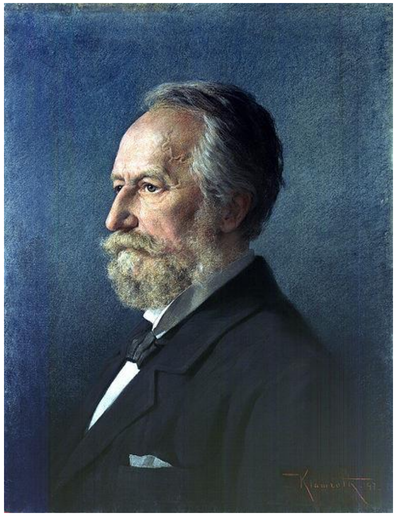
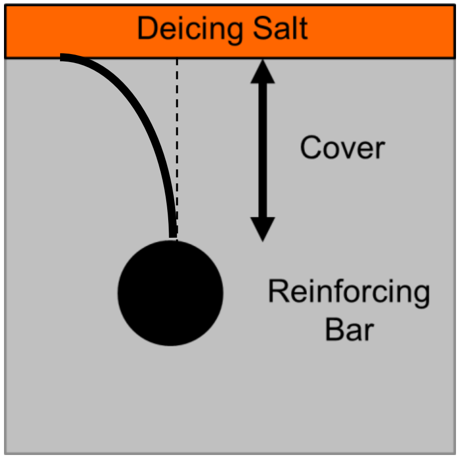
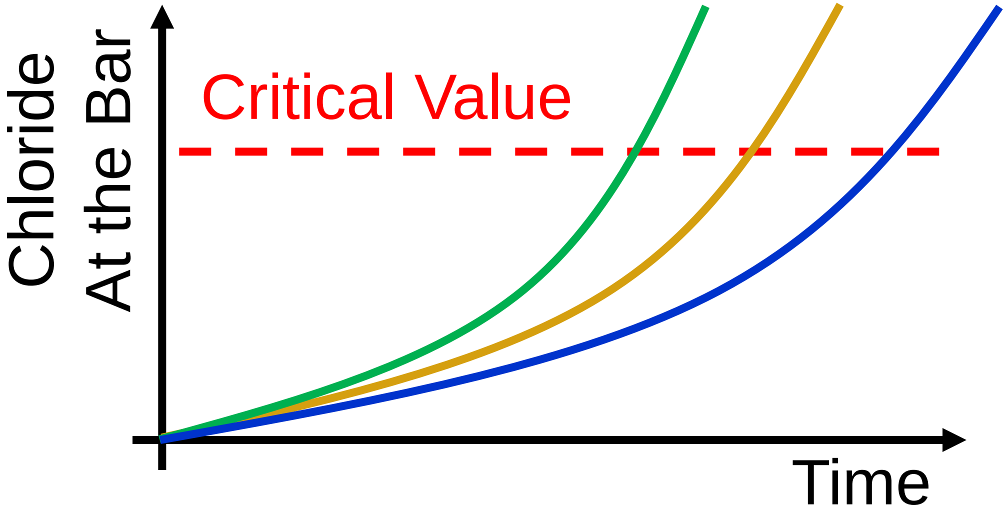
- In 1855 Adolf Fick introduced an equation (2nd law) regarding diffusion

$$\frac{\partial C}{\partial t} = \boxed{D_{Cl-}} \frac{\partial^2 C}{\partial x^2}$$

- C is the concentration, t is time, x is position, D is diffusion coefficient





# Different Modes of Transport



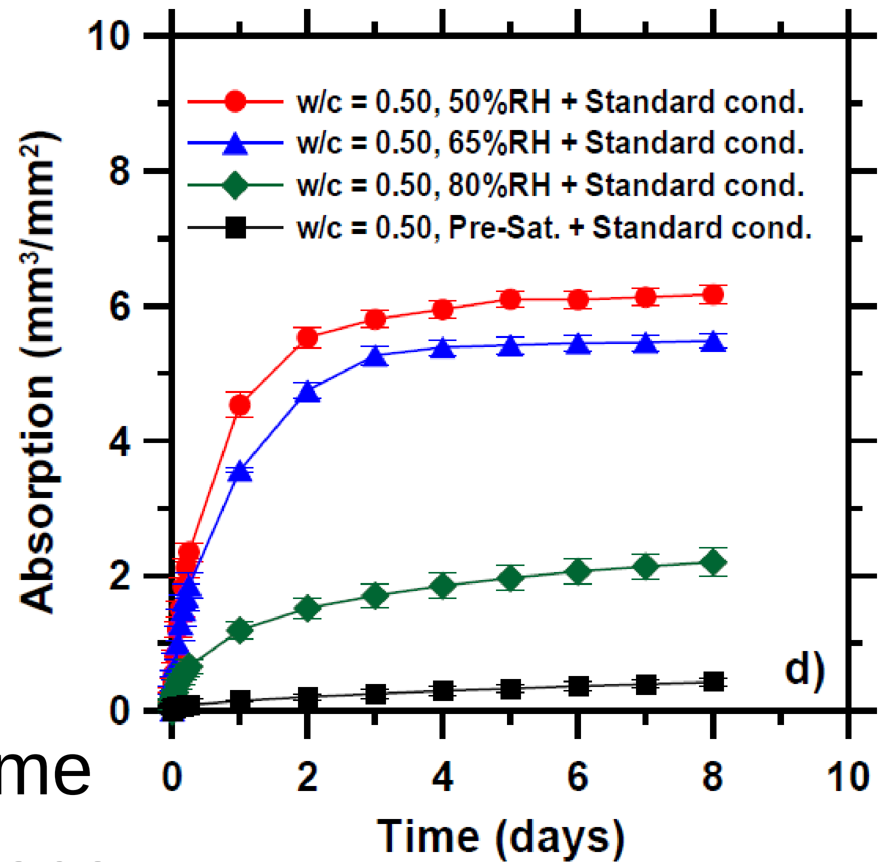
- We have discussed diffusion however there are other modes of transport
- Chlorides from deicing salts and salt water penetrate concrete due to different transport mechanisms:
  - Absorption
  - Permeation
  - Diffusion
  - Wicking

- Modifications occur due to time, binding, cracking/flaws, curing

# Absorption – Pore Filling



- Fluid can be absorbed into unsaturated concrete
- Fast when compared to other mechs.
- Modeled using square root of time
- Fills in near surface especially if poorly cured very, very fast




Castro et al. 2010

# Permeation – Pressure Driven



$$Q = K\,\frac{A(\Delta P)}{L\eta}$$


$Q$ – Rate of Flow $\left(\frac{cm^3}{s}\right)$

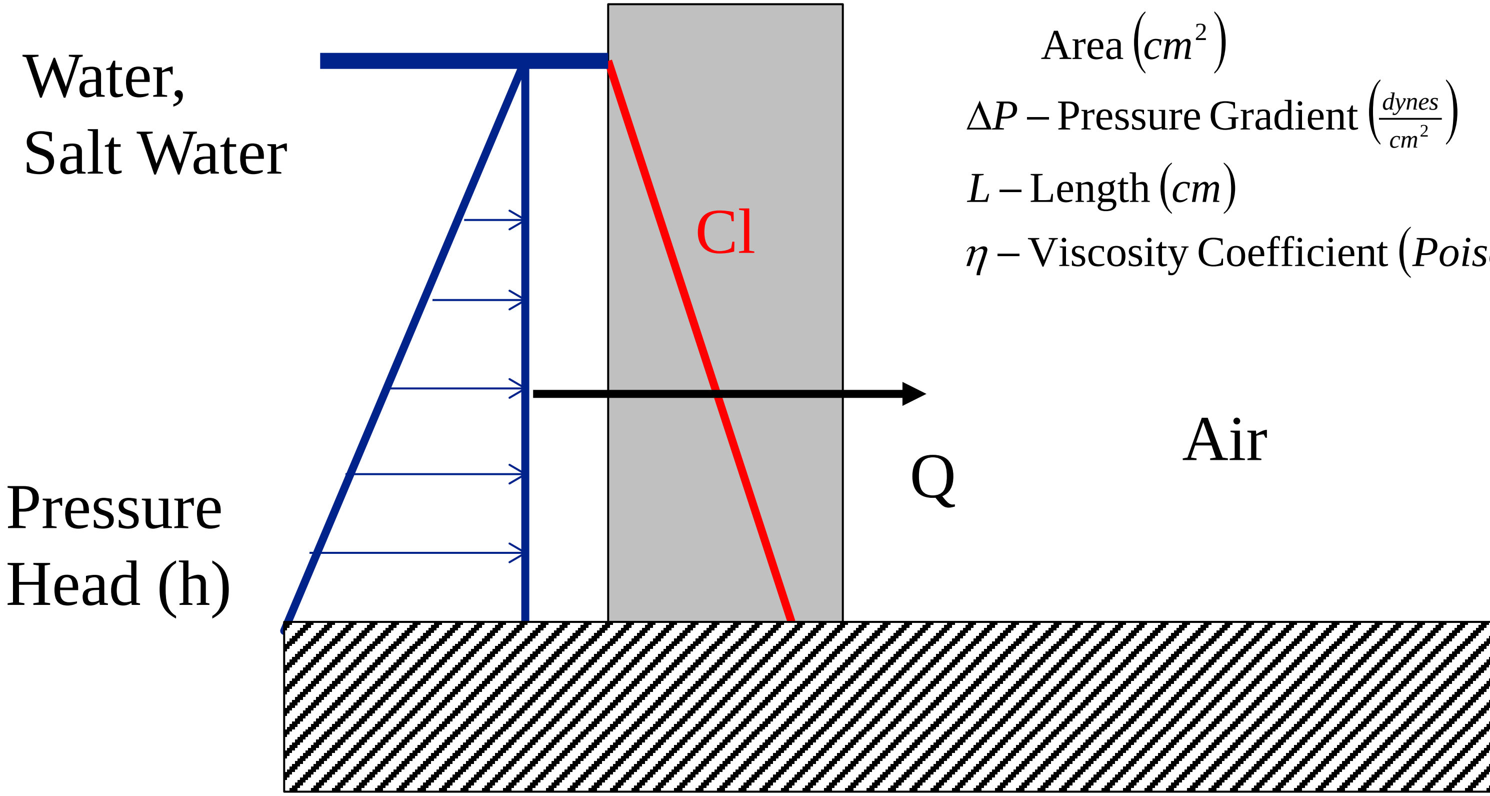
$K$ – Permeability Coefficient $(cm^2)$

$A$ – Cross Sectional Area $(cm^2)$

$\Delta P$ – Pressure Gradient $\left(\frac{dynes}{cm^2}\right)$

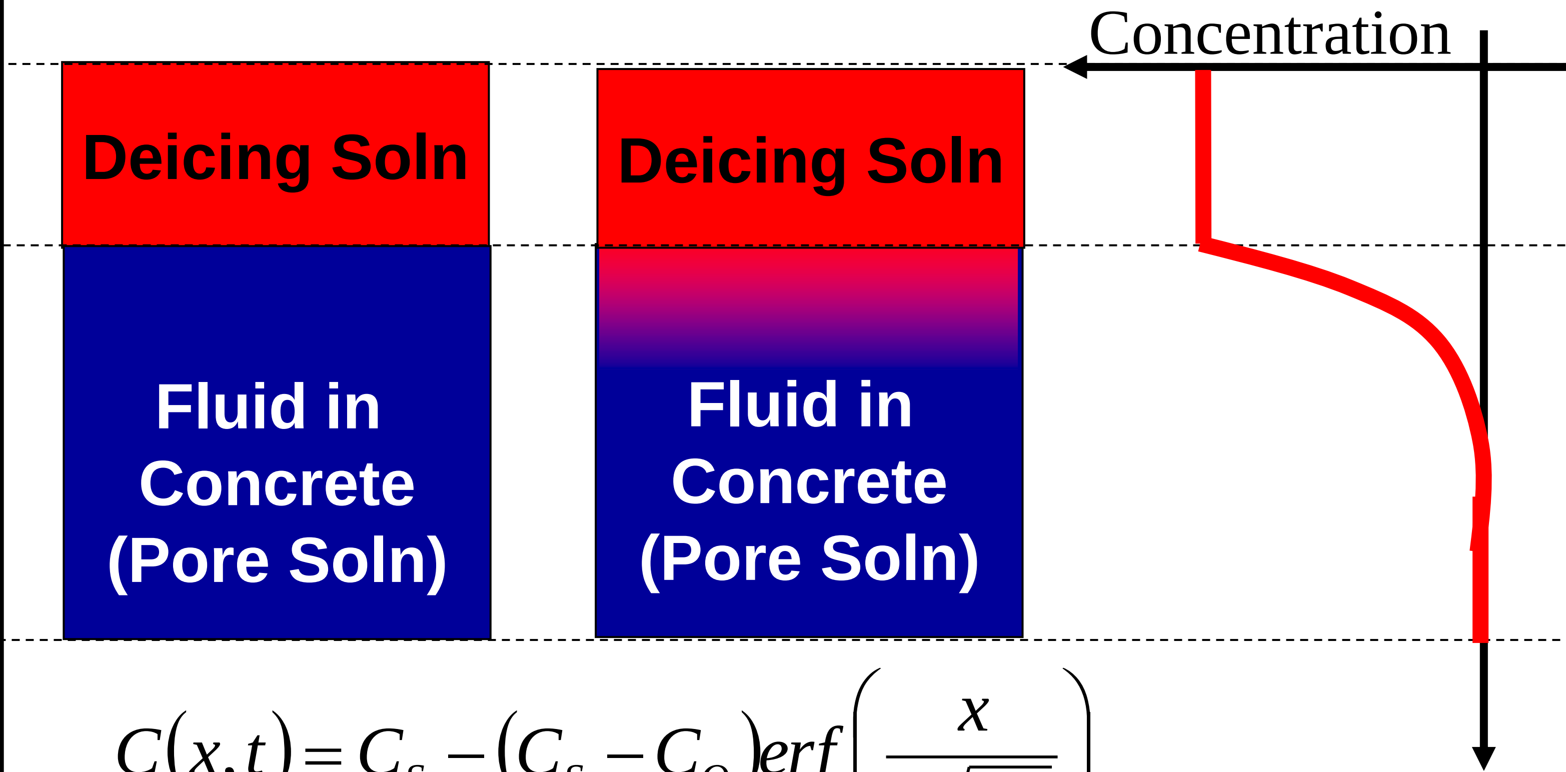
$L$ – Length $(cm)$

$\eta$ – Viscosity Coefficient $(Poise)$



# Diffusion – Concentration Driven





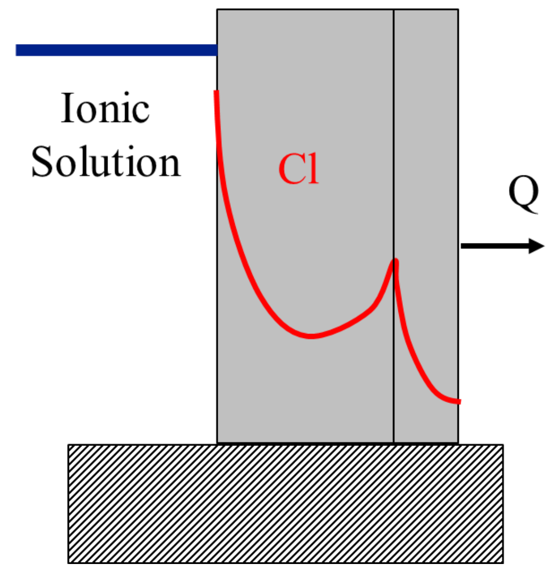

$$C(x,t) = C_S - (C_S - C_O)\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$C_S$ – Surface Concentration

$C_O$ – Background Concentration

# Wicking Action

- One side of element is exposed to a soln that contains ions and the other is open to the air, solution will be absorbed and migrate to a sharp wet front near the air surface
- Water will evaporate at a rate determined by vapor diffusion and the RH of the air
- The ionic species will precipitate out at the evaporative front




$$Q = \frac{\eta\rho}{L}\left[\frac{S^2}{2} - D_W \ln\left(\frac{\rho - C_X}{\rho - C_L}\right)\right]$$

# Review of Transport Mechanisms

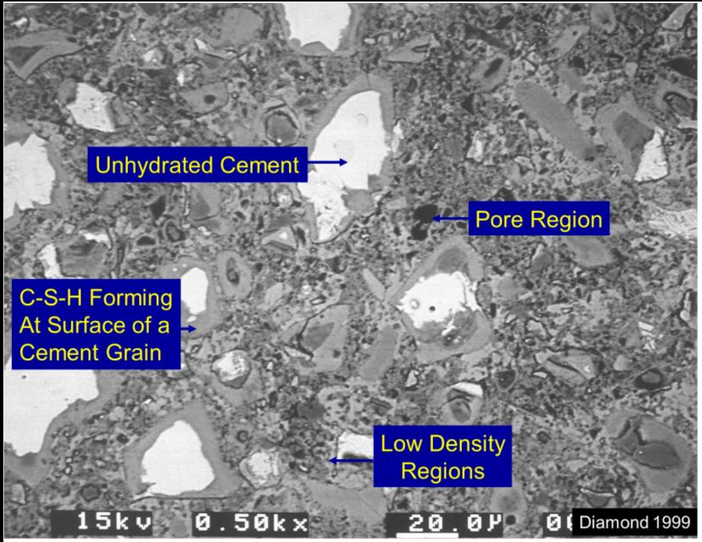


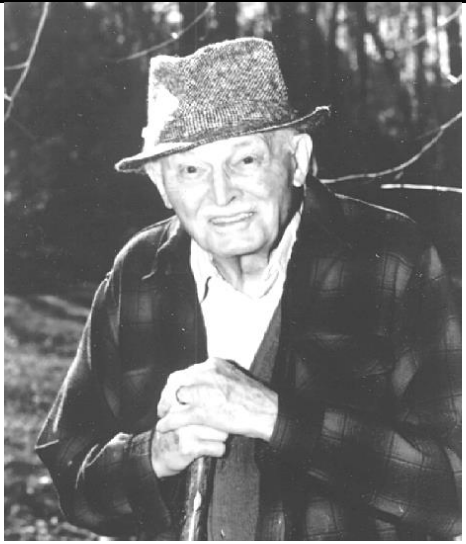
Chlorides from deicing salts and salt water penetrate concrete due to transport:

- Capillary sorption – filling of a dry material mainly due to capillary effects
- Permeation – driven by pressure gradient
- Ionic diffusion – concentration driven, diffusion of ionic species
- Wick action – drying on one side of element
- Different properties than normally measured – its not strength or slump but can be done

# We Need to Understand Structure and Sample Conditioning



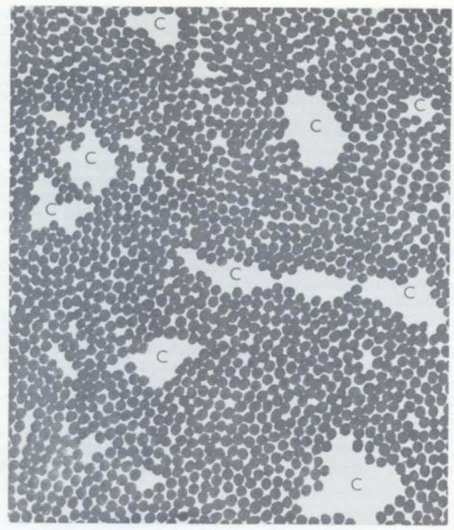



Gel Pores (2-5 nm) – small, independent of w/c, increase in volume with hydration

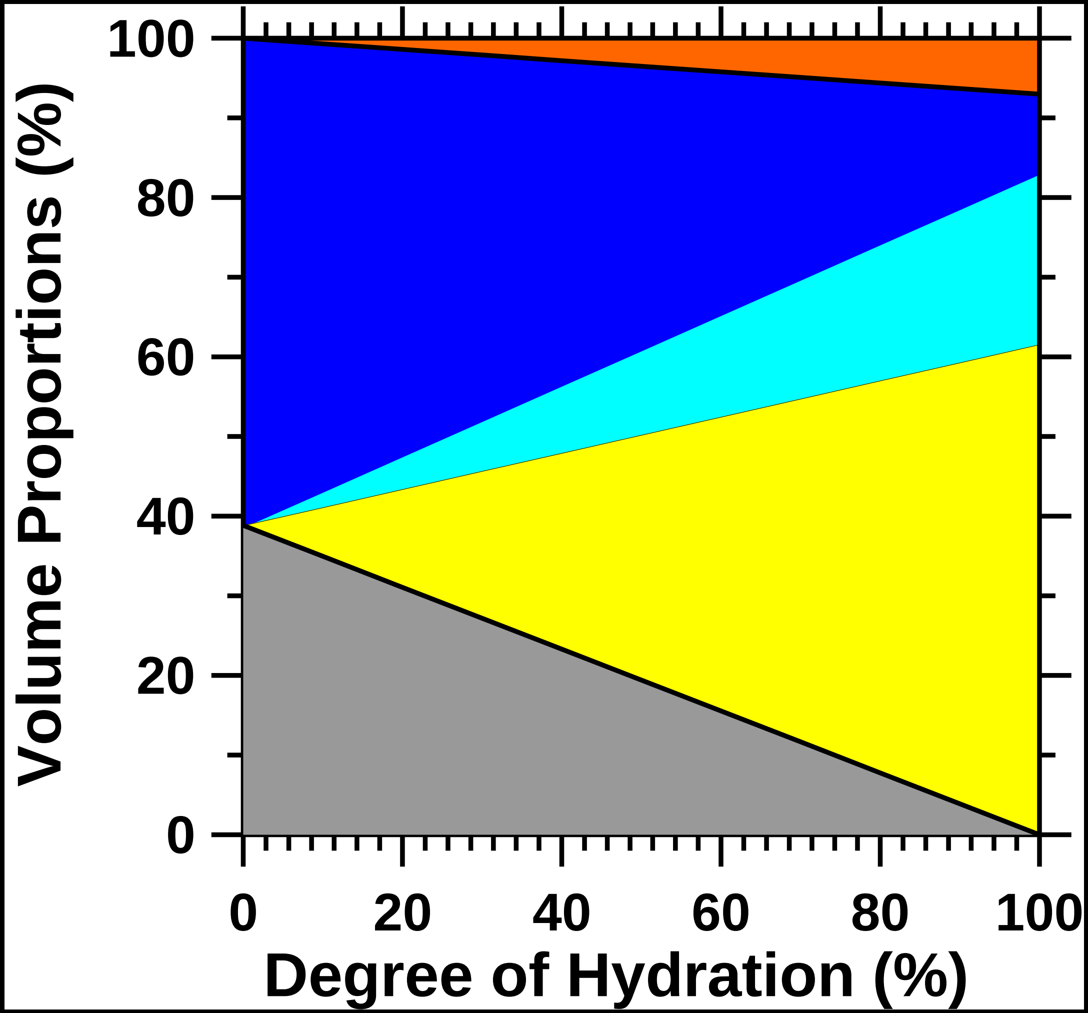
Capillary Pores (5nm-10 µm) – large pores, very dependent on w/c, decrease in volume with hydration, what we control

Entrained/Entrapped Air – Largest pores from mixing, stabilizing bubbles



# Graphical Version of Powers Model Water to Cement Ratio = 0.50






- Chemical Shrinkage
- Water Capillary Pores
- Gel Water
- Hydrated Products
- Cement

# Transport – Think Tony Saprano

Need for a New Approach

Transport Mechanisms

**Pore Structure & Degree of Sat.**

Gas Transport (Perm & Diff.)

Diffusion Using Fick's Second Law

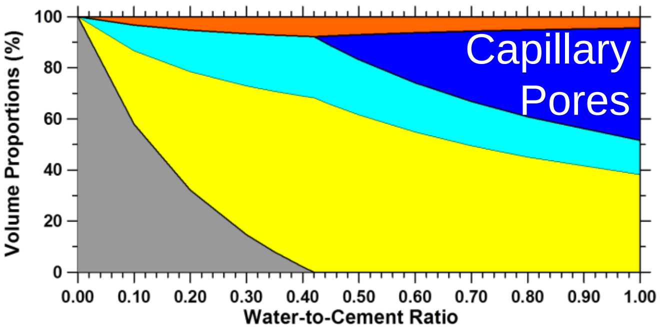
Electrical Props Factors of Interest

Accelerated Curing

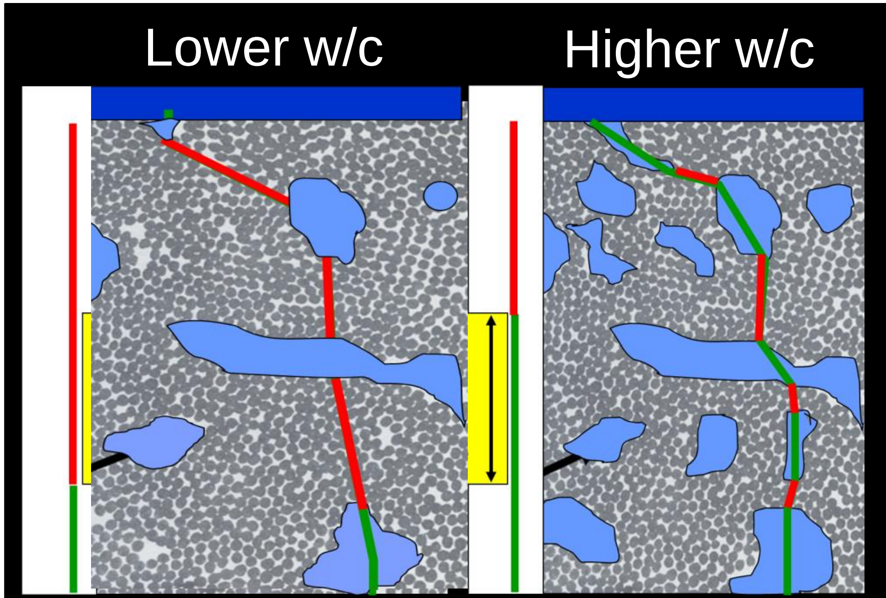
Absorption

Summary & Recommendation

- Transport mainly in large pores
- Capillary pores are large and connected
- W/C, SCM and Curing: Influence Capillary Porosity



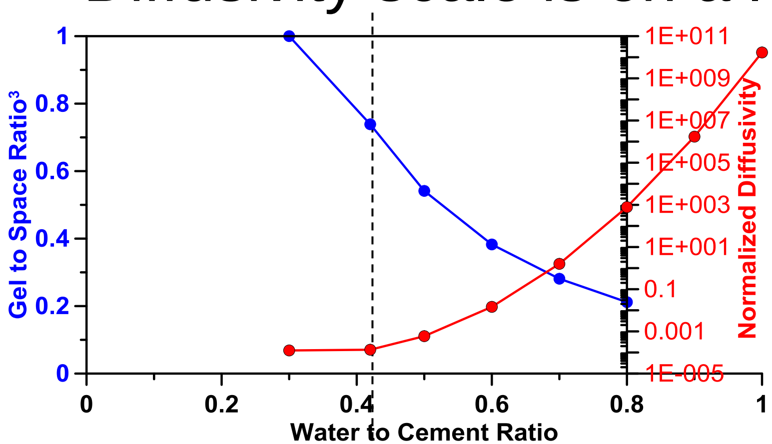

Assumes 100% Hydration

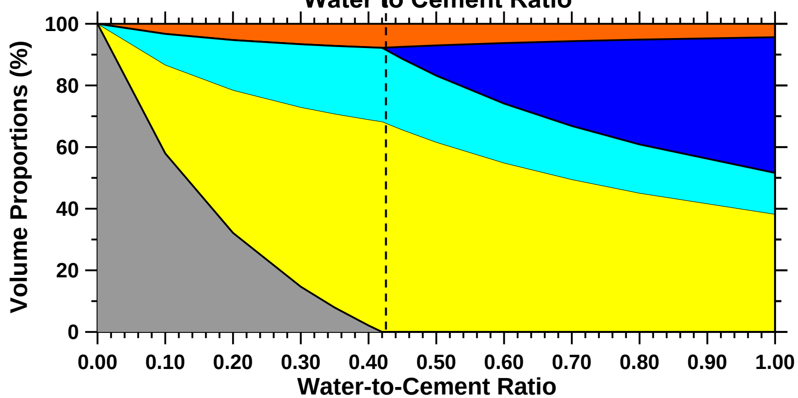


# Influence of the Water to Cement Ratio – Very Very Important

- Need for a New Approach
- Transport Mechanisms
- **Pore Structure & Degree of Sat.**
- Gas Transport (Perm & Diff.)
- Diffusion Using Fick's Second Law
- Electrical Props Factors of Interest
- Accelerated Curing
- Absorption
- Summary & Recommendation

- 0.42 in sealed system (0.36 water cured)
- Gel to space ratio cubed (~f'c) (w/ updating space)
- Diffusivity scale is on a log scale

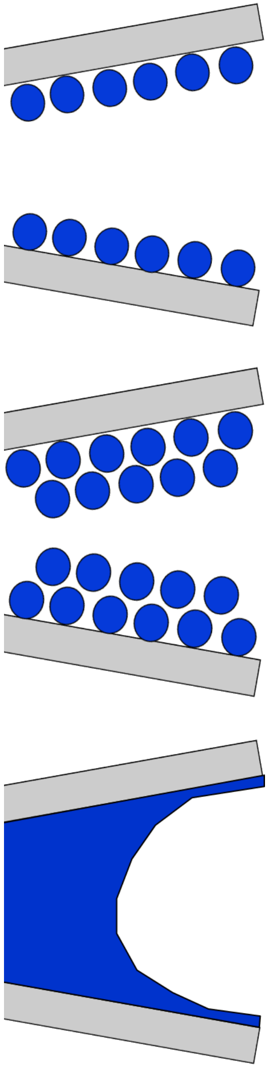



# The Role of Water (Degree of Saturation) in The Microstructure



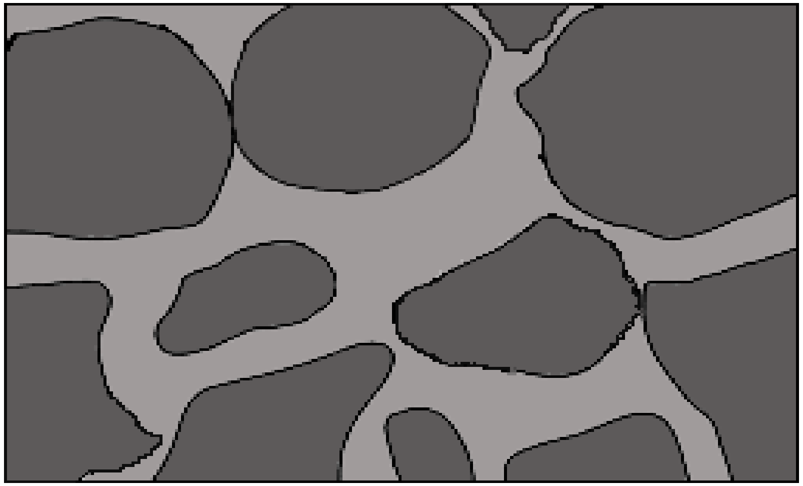
- Assume we start with a dry sample water will attach to the surface of the pores
- As RH increases the water molecules begin to develop in layers on the surfaces
- Above RH 45 to 60% RH the water starts to fill in the pores forming a meniscus
- At 80% RH Capillary pores begin to fill in



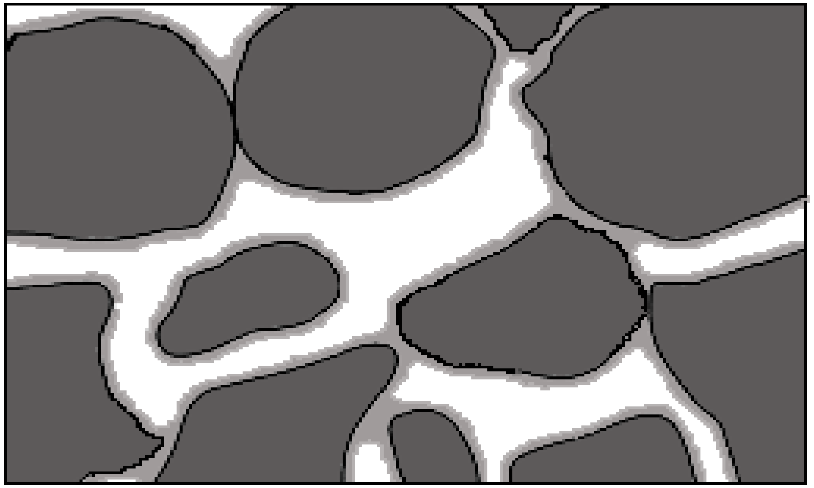
# Degree of Saturation and Its Impact on Transport



- 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**

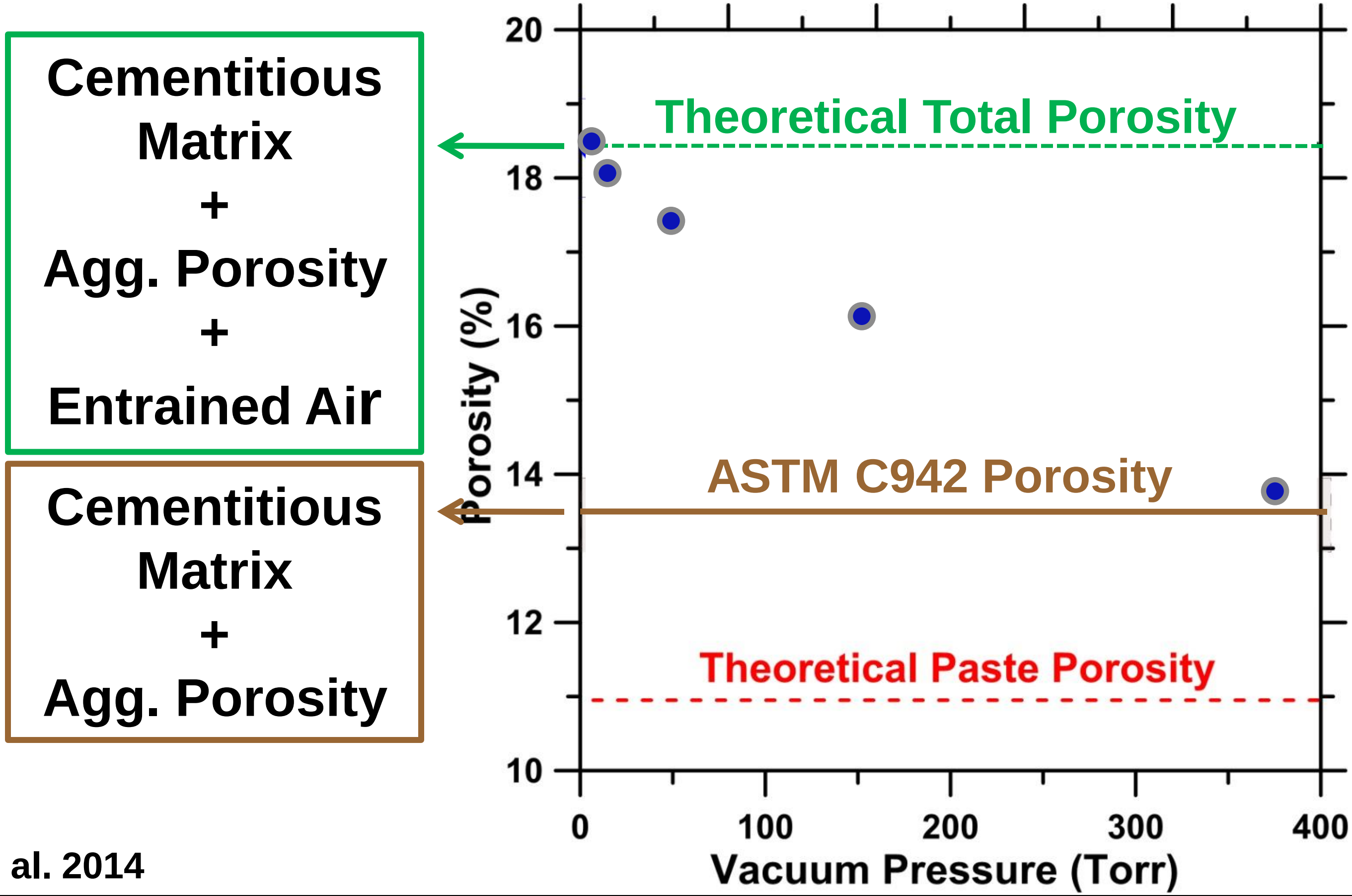


**Drying**

# Important Discussion Regarding the Degree of Saturation (DOS)



- Began with an INDOT Class C Bridge Deck Mixture (air entrained w/c 0.42)

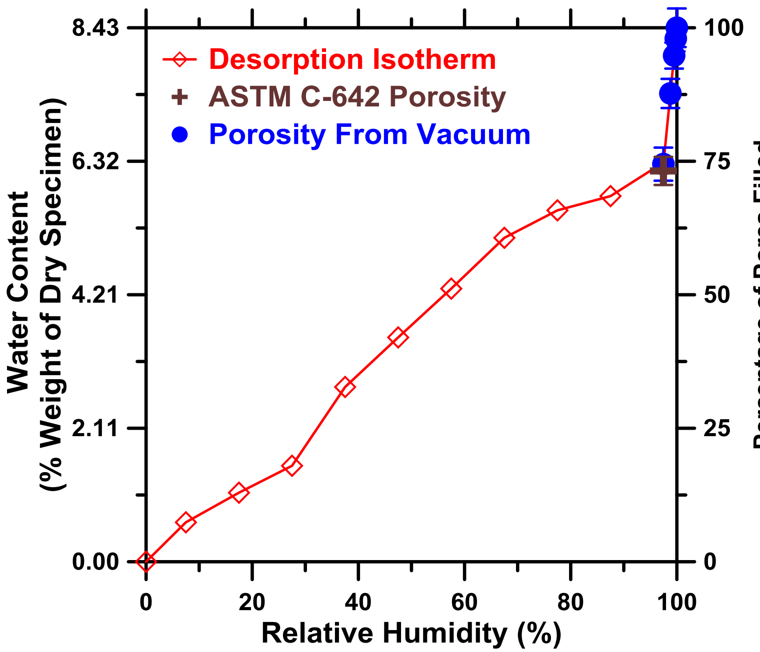



Bu et al. 2014

# Porosity Testing Methods



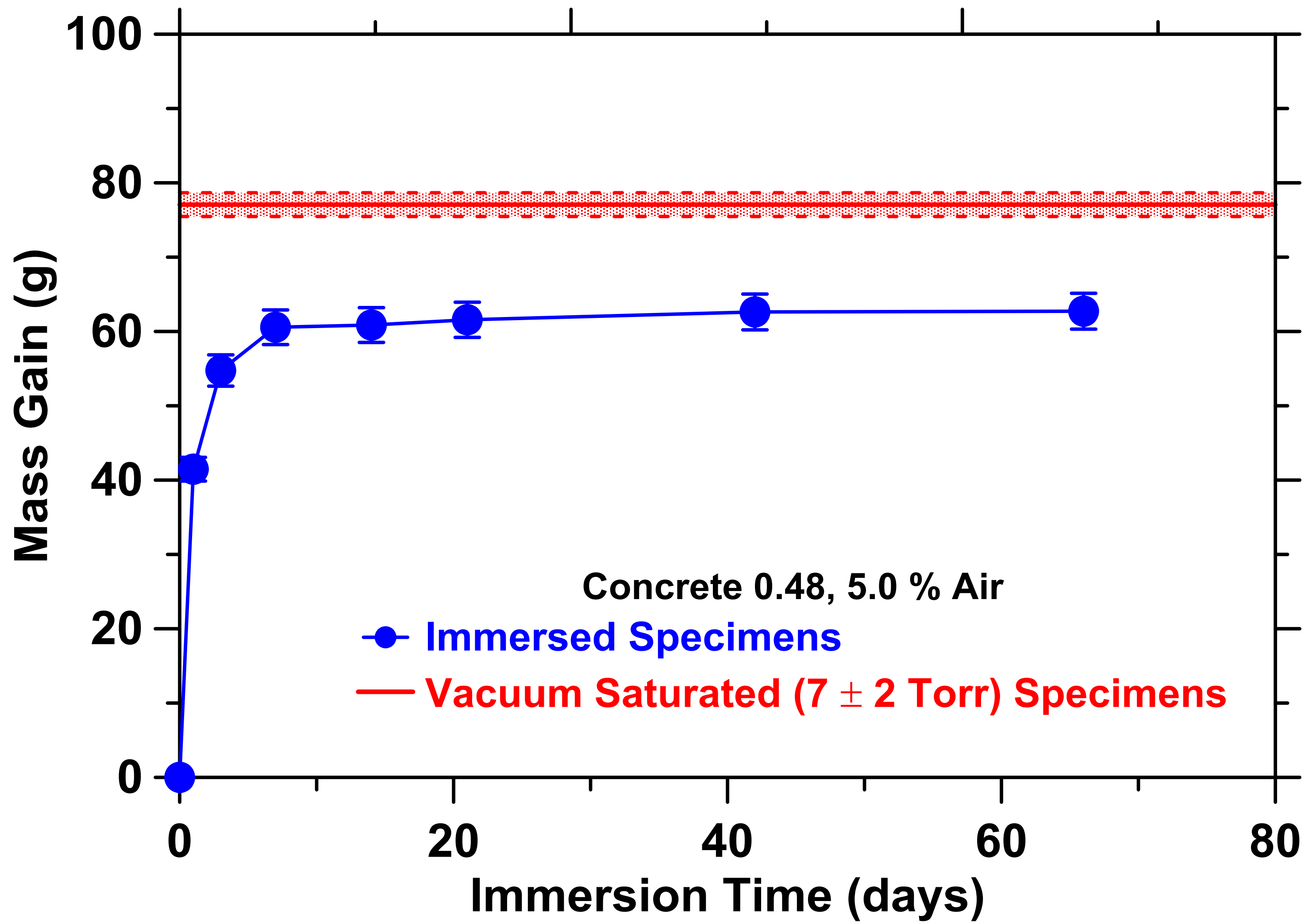
- ASTM C642 does not measure the complete pore volume in concrete
- The level of vacuum used can be very important for determining DOS
- ASTM C642 and low vacuum does not fill entrapped/ entrained air voids
- DOS and RH are not linearly related




**Castro et al. 2014**

# Placing a Sample Under Water Does Not Provide Complete Saturation

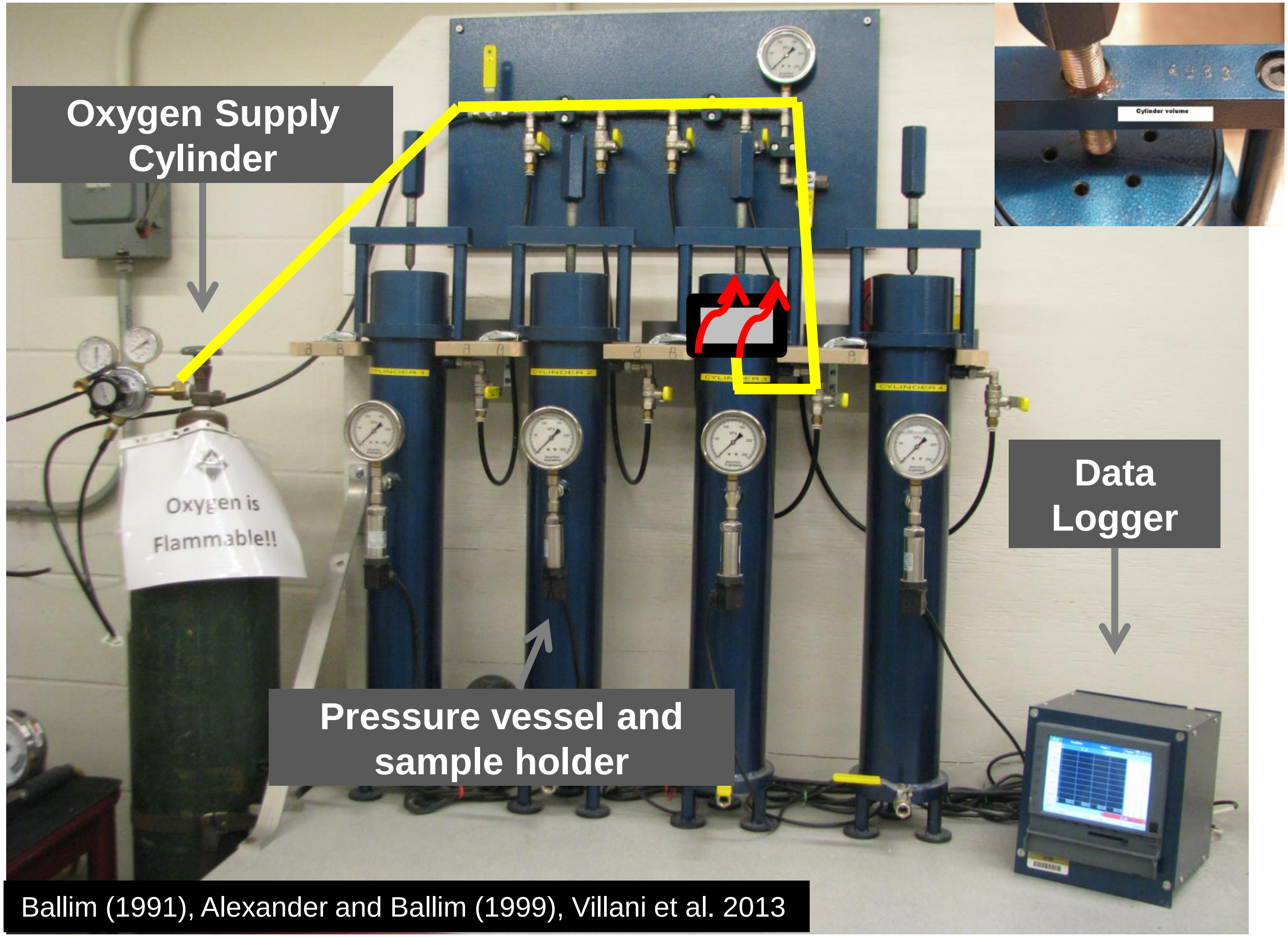





Bu et al. 2014

# Oxygen Permeability

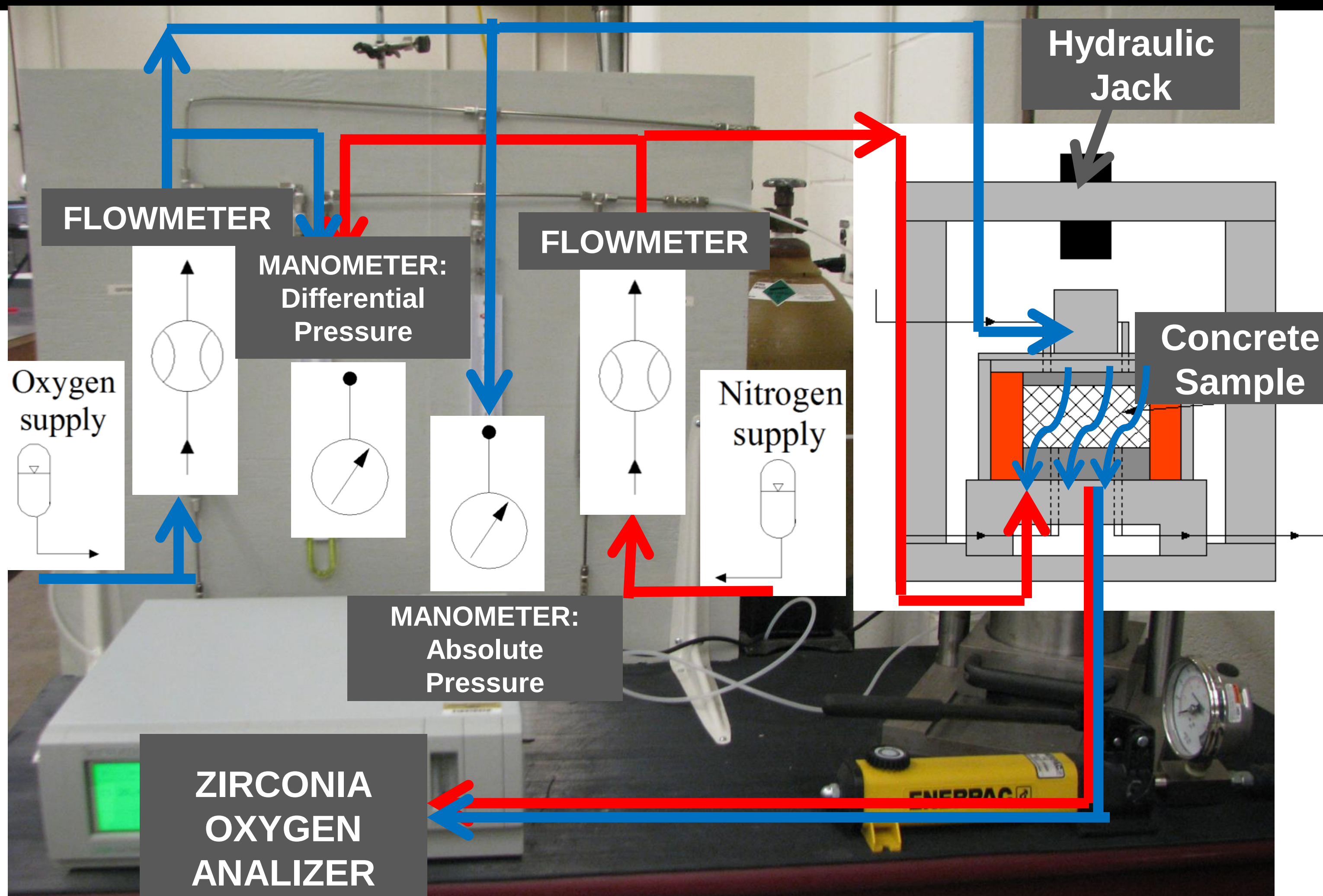





Ballim (1991), Alexander and Ballim (1999), Villani et al. 2013

# Gas Transport Testing






Lawrence (1984), Wong (2009), Villani et al. 2013

# Influence of w/c and conditioning

Need for a New Approach

Transport Mechanisms

Pore Structure & Degree of Sat.

**Gas Transport (Perm & Diff.)**

Diffusion Using Fick's Second Law

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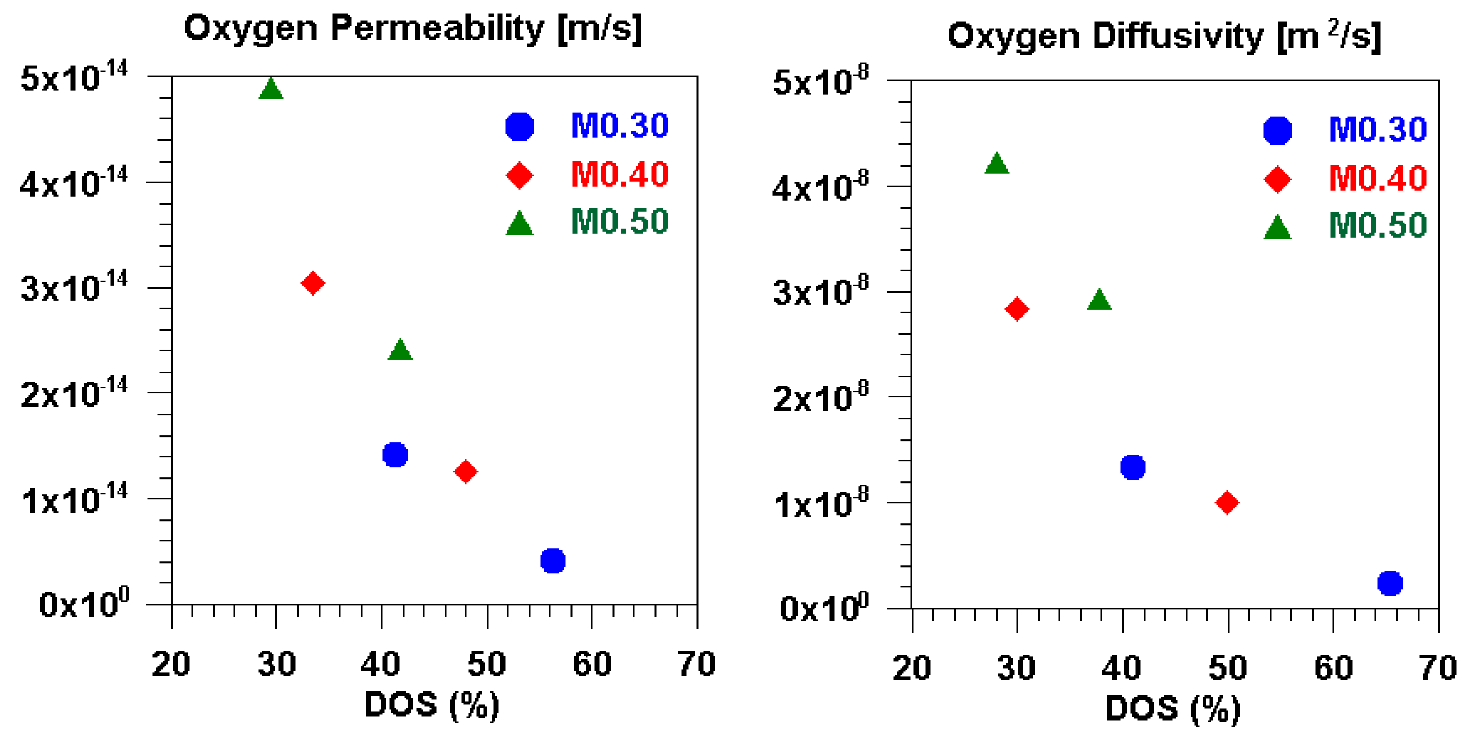
Absorption

Summary & Recommendation




- Decrease in w/c causes a decreases in gas transport (reduction of total porosity and connectivity)
- Increase of degree of saturation (DOS) reduces gas transport (less pore space is available for gas transport)
- Even gel porosity play a role

Villani et al. 2013

# Inter- and Intra-Laboratory variability

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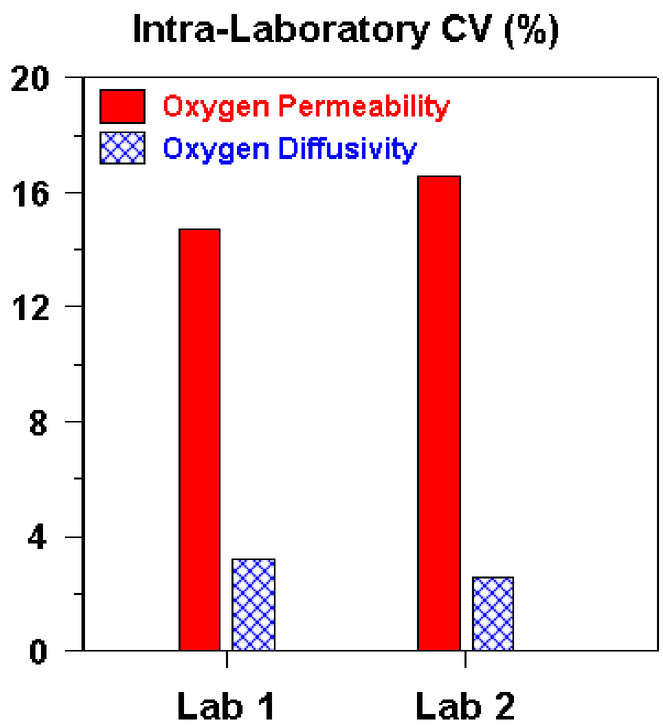
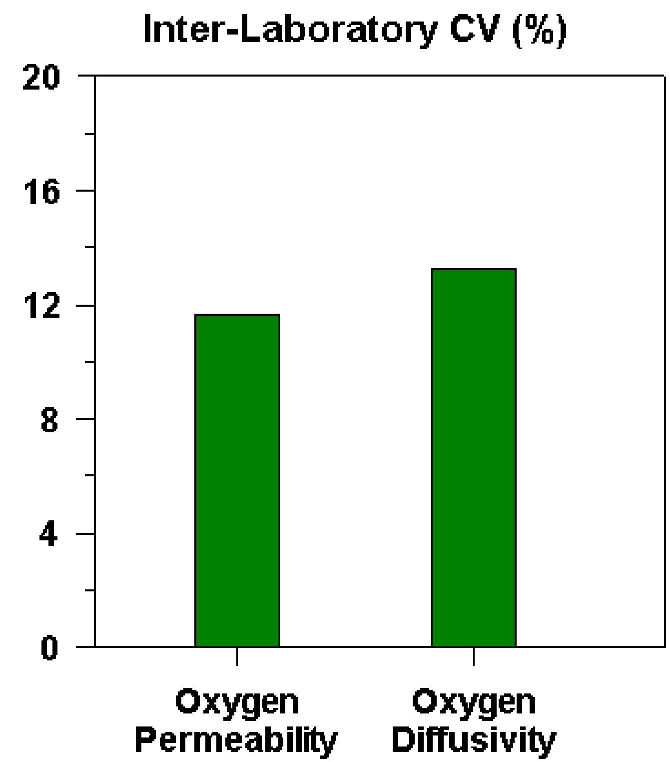
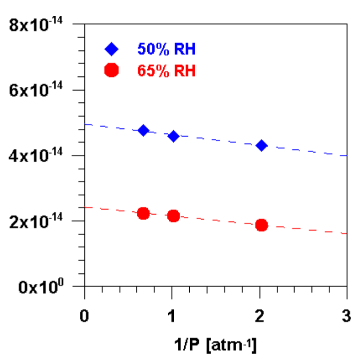



This variation can be attributed to variations in pressure in the testing device (at first step)

**Villani et al. 2013**

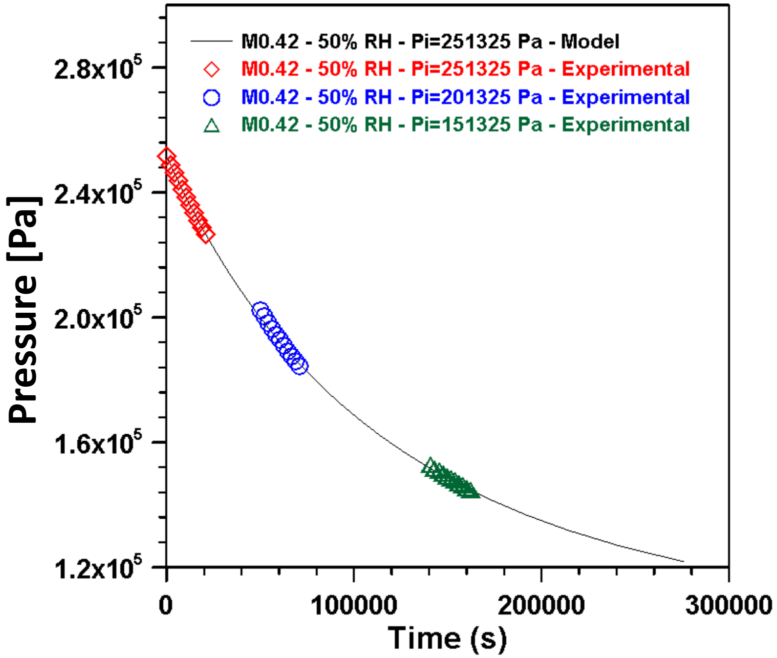
# Influence of Pressure Rederived from Fundamental Principles (Villani 2014)



## Current Formulation

- Used by many
- Non unique k value

$$k_{SA} = \frac{M\,V_v\,L\,g}{R\,T\,\Delta t\,A} ln\frac{P_0}{P_v}$$




## Proposed Approach

**Darcy's Law (compressible fluids)**

$$v_D = -\frac{k}{\mu}\frac{\partial P}{\partial z}$$

**Ideal Gas Law**

$$m = \frac{M\,V_v\,P}{R\,T}$$

**Continuity equation**

$$\frac{\partial \rho}{\partial t} + \nabla \rho v_D = 0$$

**Intrinsic Permeability**

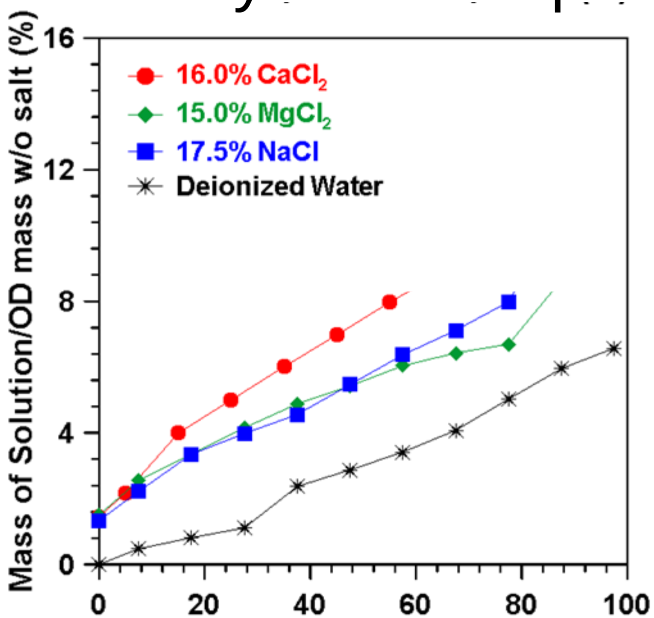
$$k_{in} = \frac{\operatorname{atanh}\left(\frac{P_0}{P}\right) - \gamma}{\chi\ t\left(1 + \frac{b}{P}\right)}$$

Villani 2014

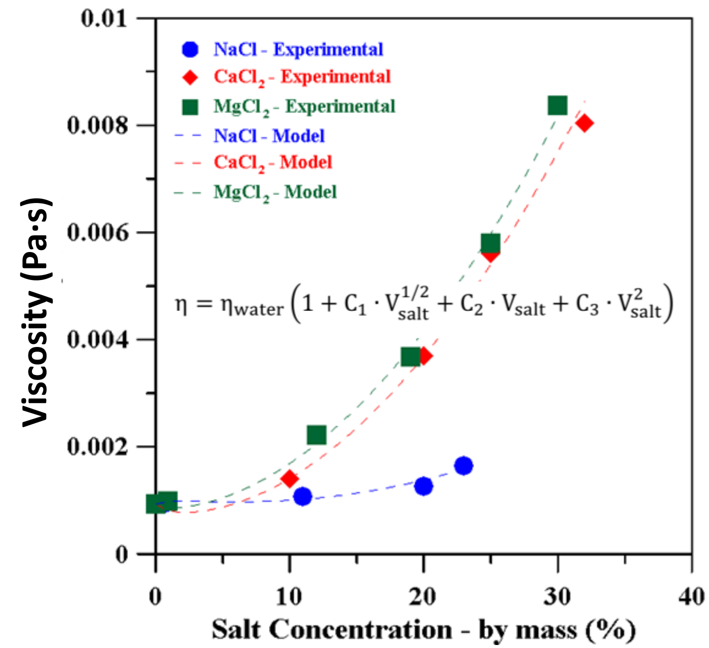
# Interesting Aside Regarding Fluid Properties



- Salts alter the degree of saturation which in turn can influence transport (activity)
- Salts also alter surface tension and viscosity of the fluid which can change sorption rates
- Reactivity is also important (Farnam in prep)



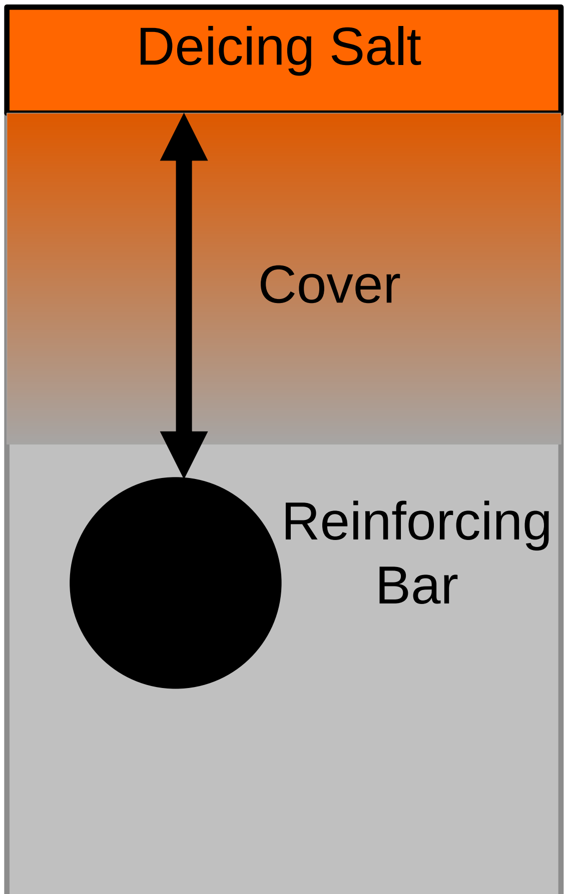

Villani et al. 2013



# Chloride Ingress
# Fick's Second Law



- Concrete protects steel from deicing salts




Loading due to Exposure

$$1 - erf\left(\frac{x}{\sqrt{4Dt}}\right) = \frac{Cx - Co}{Cs - Co}$$

Material and Geometry

- x - distance from surface
- t - time
- C - chloride concentration
- D is a material property that describes the diffusion rate

# Ficks Second Law ASTM C 1556

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**Diffusion Using Fick's Second Law**

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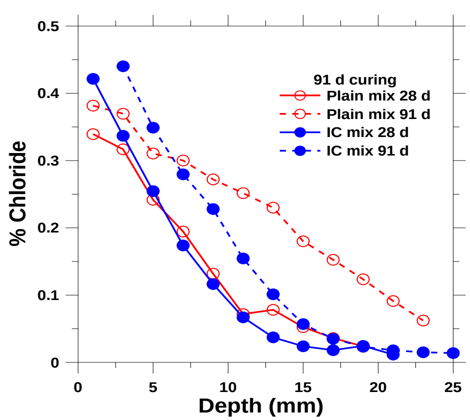
## Epoxy Coating


## Immersion

## Grinding

**Fitting with** $$\frac{C_{x,t} - C_0}{C_s - C_0} = erfc\left(\frac{x}{2\sqrt{D_{APP} t}}\right)$$



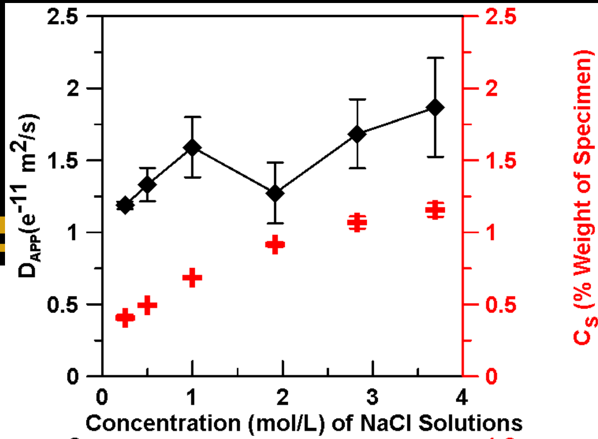

**$C_s$ and $D_{APP}$**

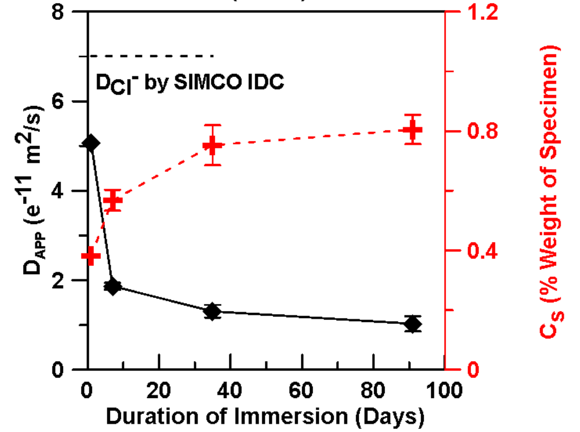
## Titration

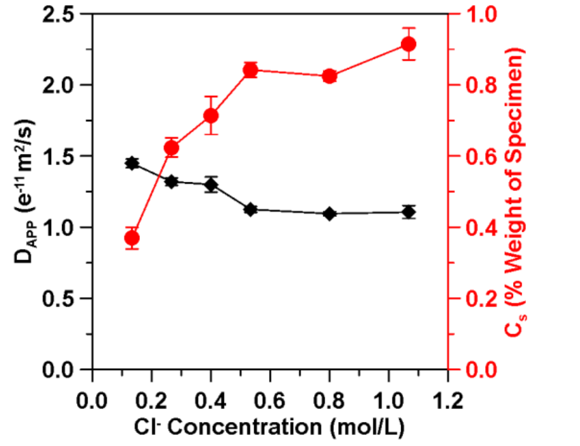
# Ponding Results

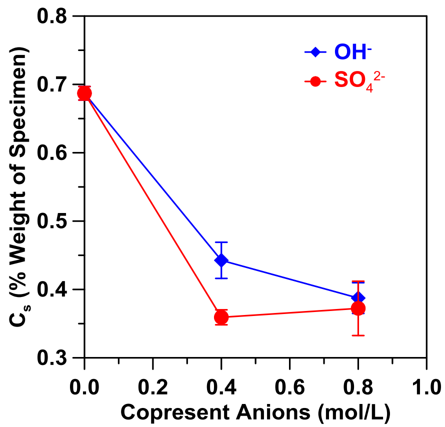


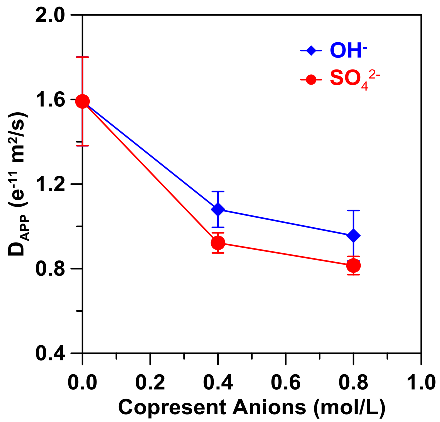
- $D_{APP}$ and $C_S$ are clearly not material properties
- Concentration, Time, Seawater Concentration, and Co-Present Ions
- Take substantial time and effort to perform




Bu et al. 2014

# Where Do We Find Tests



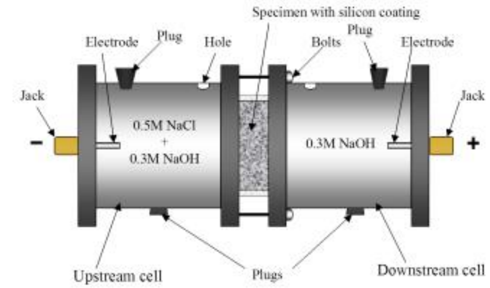
- Much like Indiana we seem to be on the impossible search for the "holy grail"

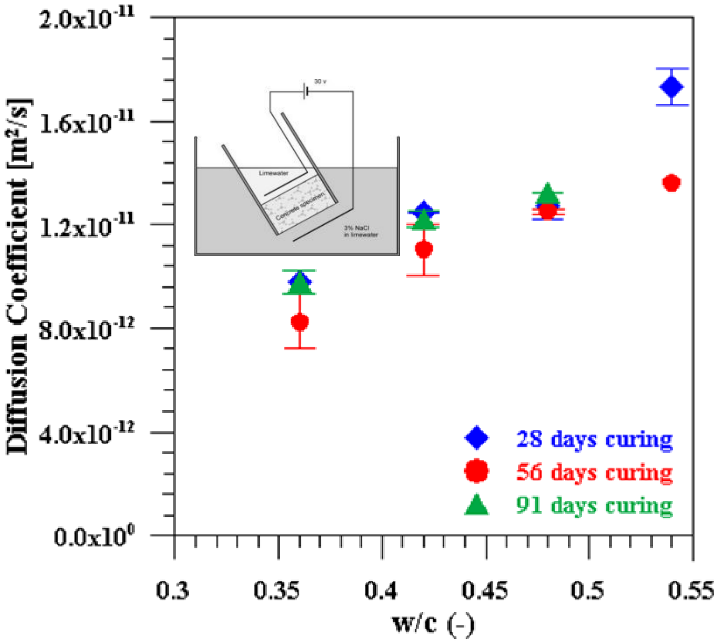
- We want a test for transport (or durability) that is fast, accurate, inexpensive easy to interpret but it also needs to be scientifically valid
- We think that electrical measurements can be a significant part of this approach

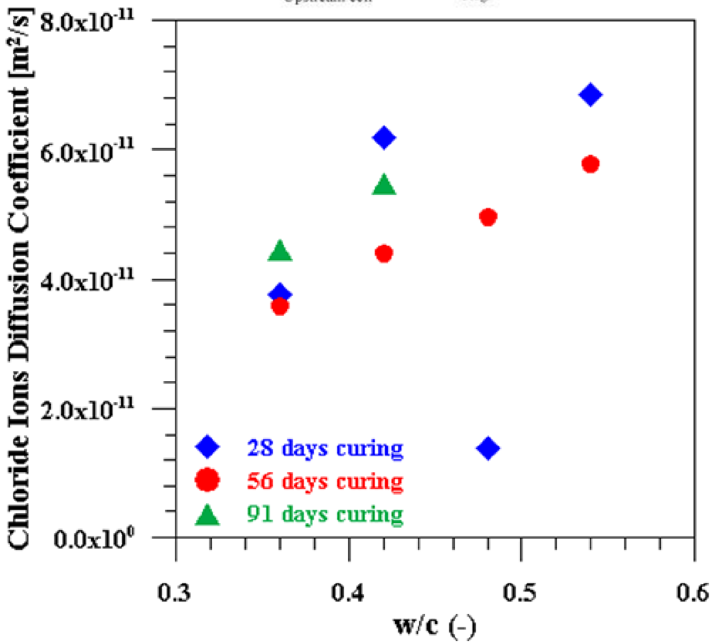
# Nord Test and Stadium



- Two popular tests that are being used in service life modeling (Nord Test) and (Stadium)



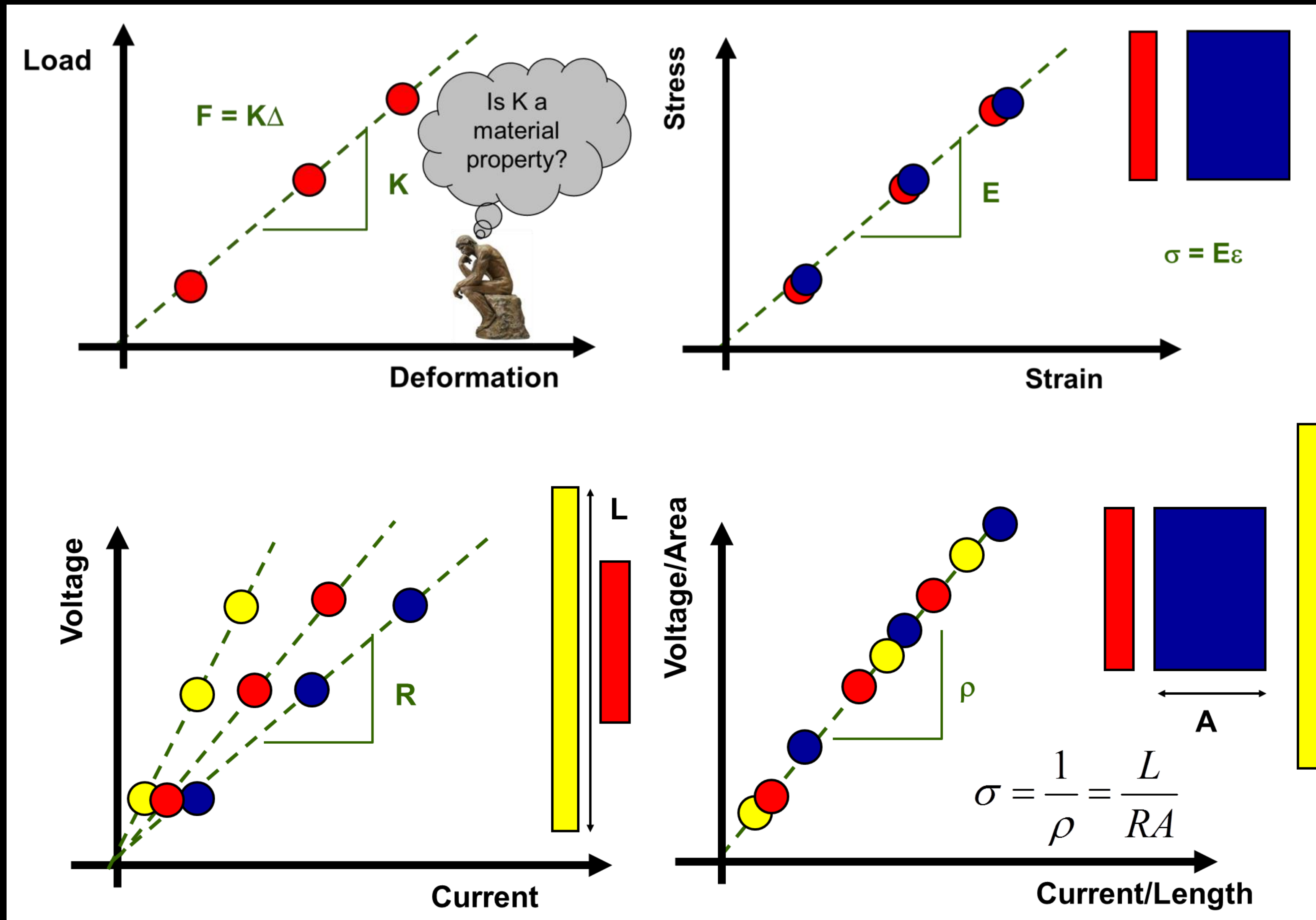




**Villani et al. 2014**

# Electrical Methods
# Food For Thought





# Lets Start with Notation and Archie



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

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

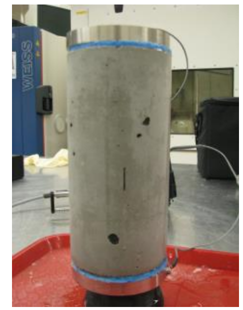

- Assume the only conductive phase is the fluid and the resistivity of the concrete is the product of resistivity of solution and the formation factor (inverse porosity and connectivity) (solutions exist for other conductive phases Weiss et al.)

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

# Rapid Test Methods

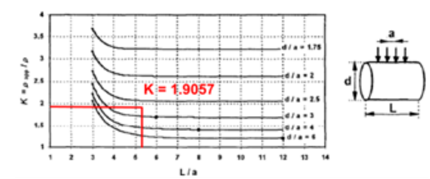


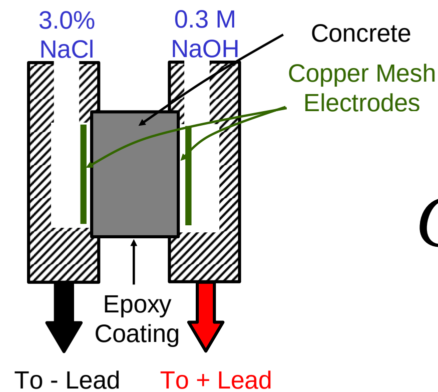
- Uniaxial, surface, embedded, and RCPT electrical measurements all yield results that can be directly compared if done properly
- Proper reporting is essential



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

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

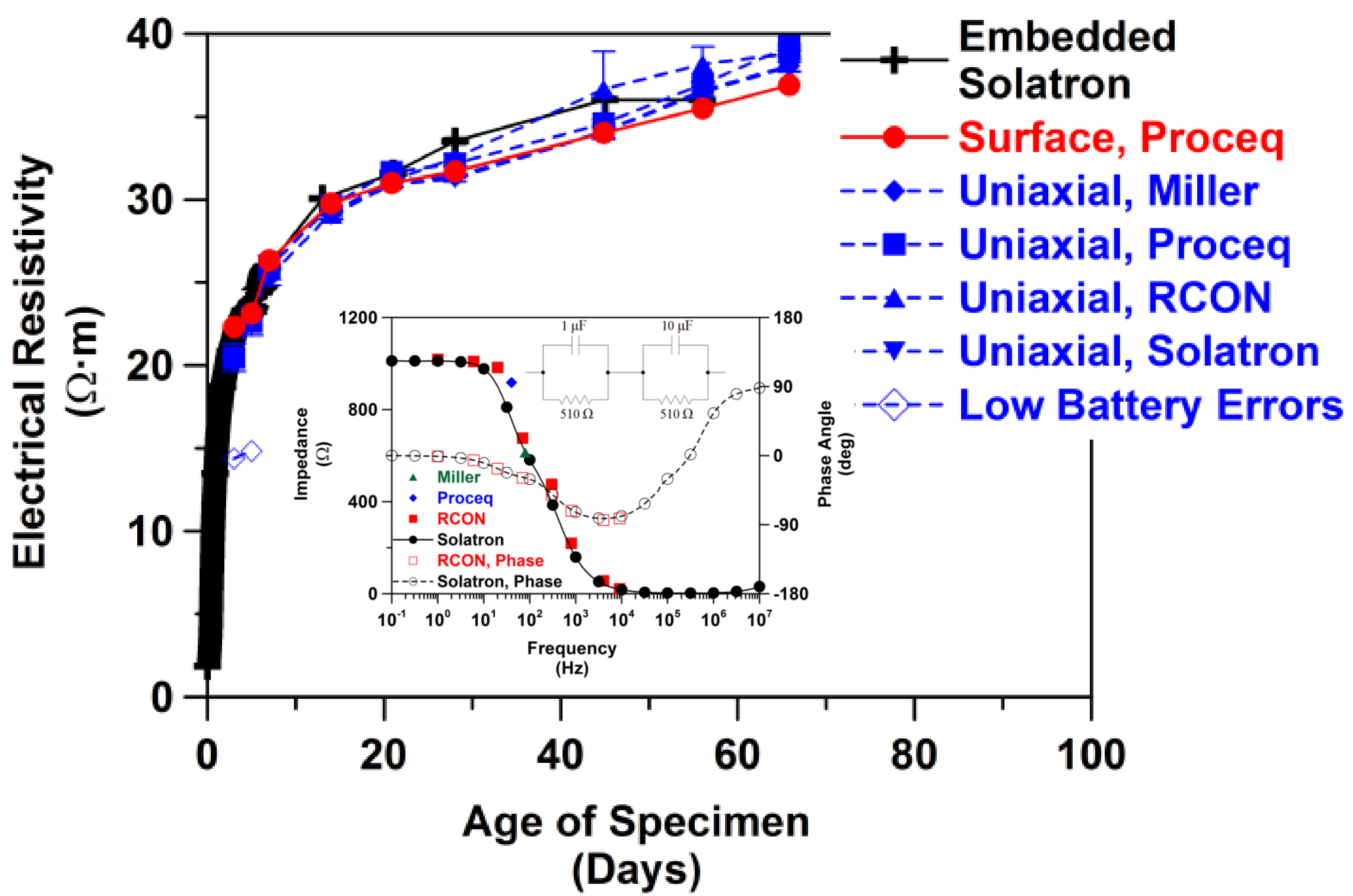



$$Q = \int_{0h}^{6h} \frac{V}{\rho\kappa} dt$$

# Comparison of Different Manufacturers



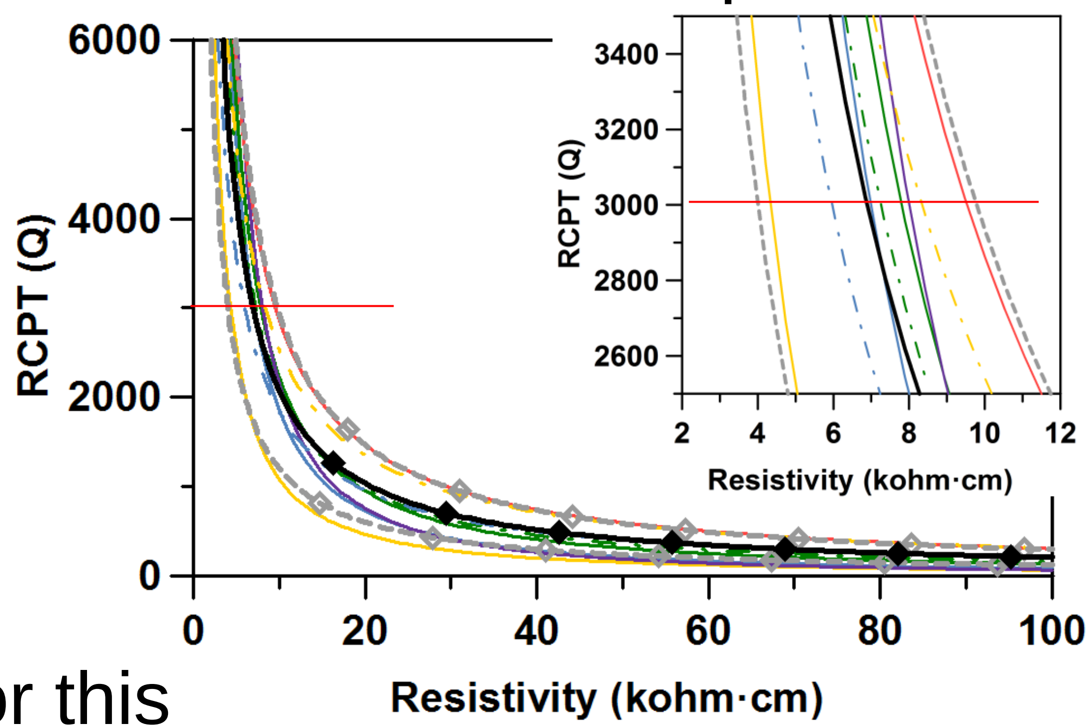



Spragg et al. 2012

# Relationship Between Q (Coloumbs) and Resistivity (ρ)



- 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



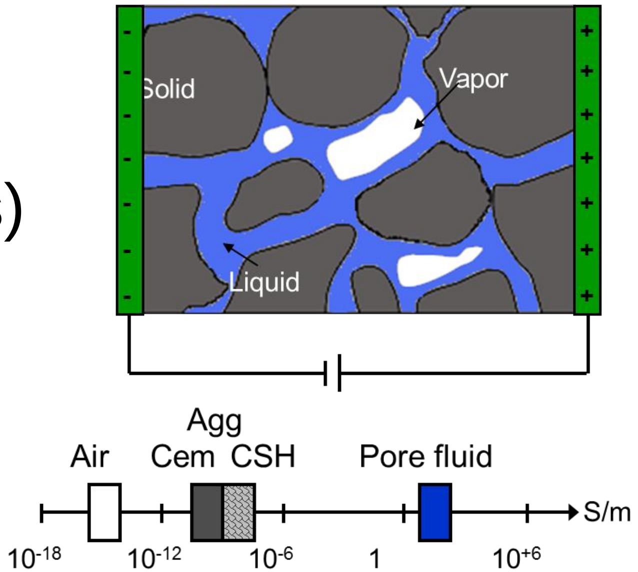

Spragg et al. 2013

# Parallel Law Modified



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

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




$\rho_{Bulk}$: concrete conductivity (S/m)

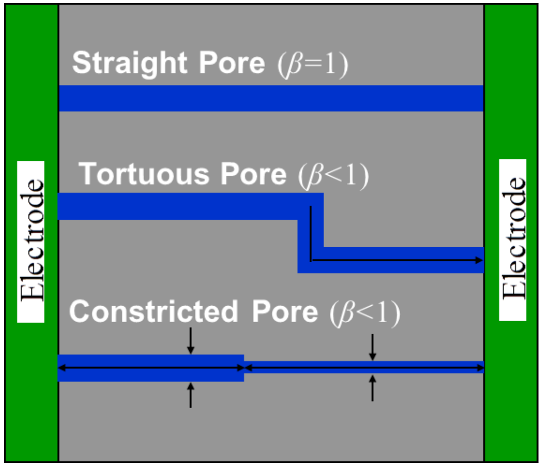
$\rho_{Pore}$: pore solution conductivity (S/m)

**F**: Formation Factor

$\phi$: pore volume fraction

$\beta$: avg. liquid connectivity (describes liquid tortuosity and constrictedness)

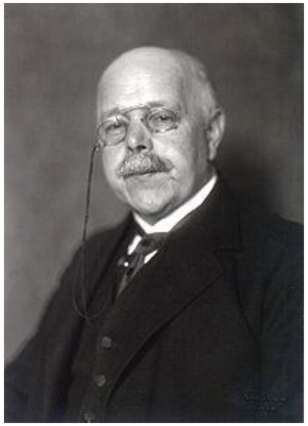
(Garboczi 1990, Christensen et al. 1994, Rajabipour 2006)

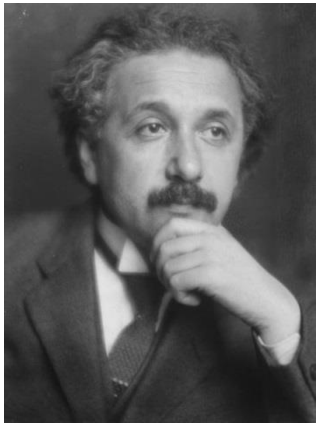


# From Resistivity to Diffusivity Nernst Einstein Relationship



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





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

Table 1 – Diffusion coefficient of various species in free water

| Species | $D_i^{\mu}$ ($10^{-9}$ 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 |

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

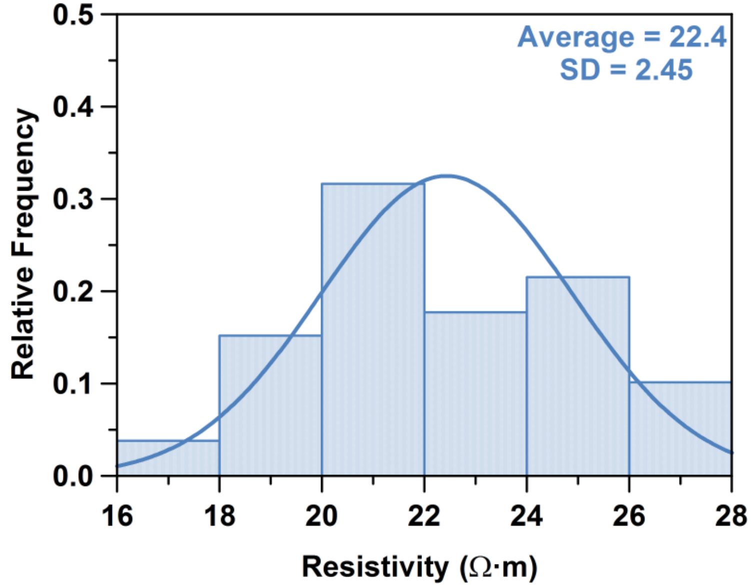
$$D_i = D_i^{\mu} \cdot \phi\beta = D_i^{\mu} \cdot \frac{1}{F}$$

# Components of Variation



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

- 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



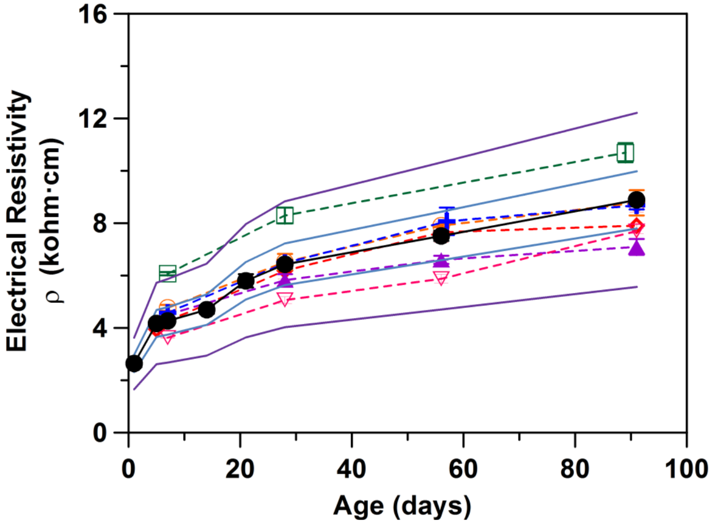

- Data shown is from a central mix plant with one mixture run frequently, low variation

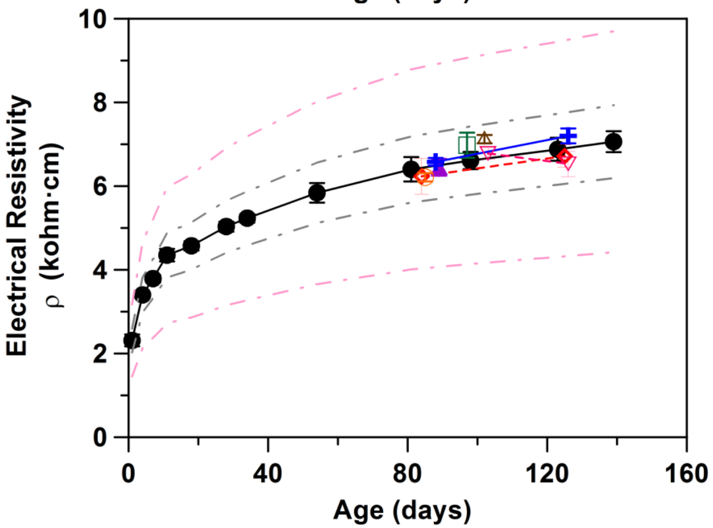
Spragg et al. 2012

# Components of Variation
# Attention to Curing is Critical



- 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



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

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

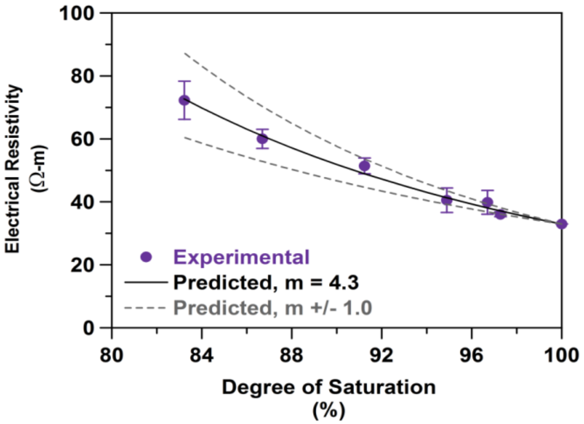
- $\rho$ is the resistivity at an equivalent age $t_{equivalent}$
- $\rho_o^*$: pore solution resistivity at saturation
- $f(S)$ saturation function
- $f(T_{testing})$ testing temperature correction
- $f(Leach)$ leaching function

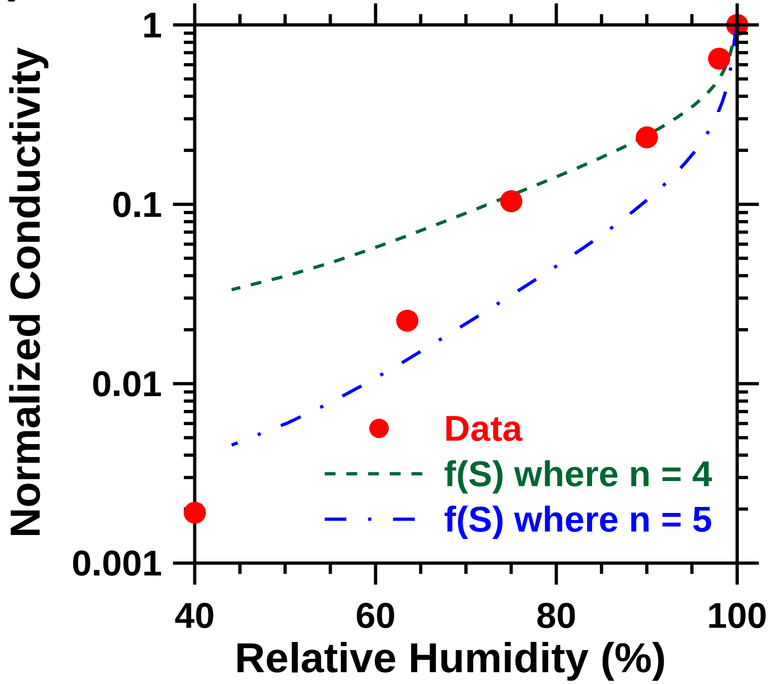
**Spragg et al. 2013**

# Saturation



- 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

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

# Testing Temperature

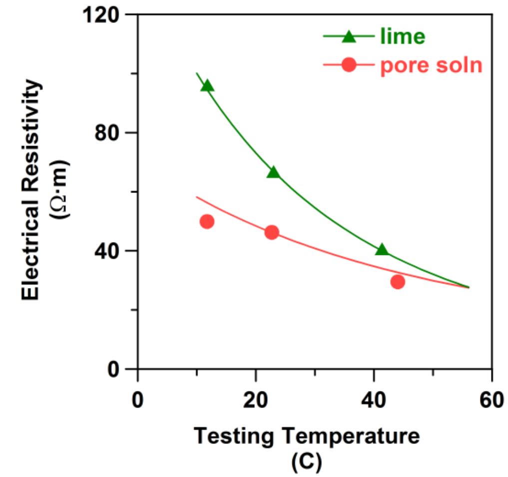


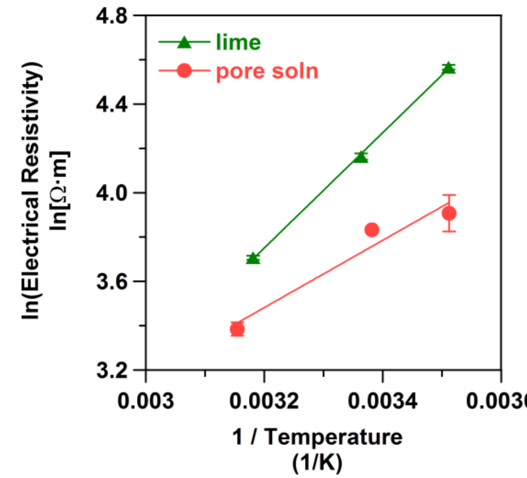
- Activation Energy of Conduction (test temp)

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



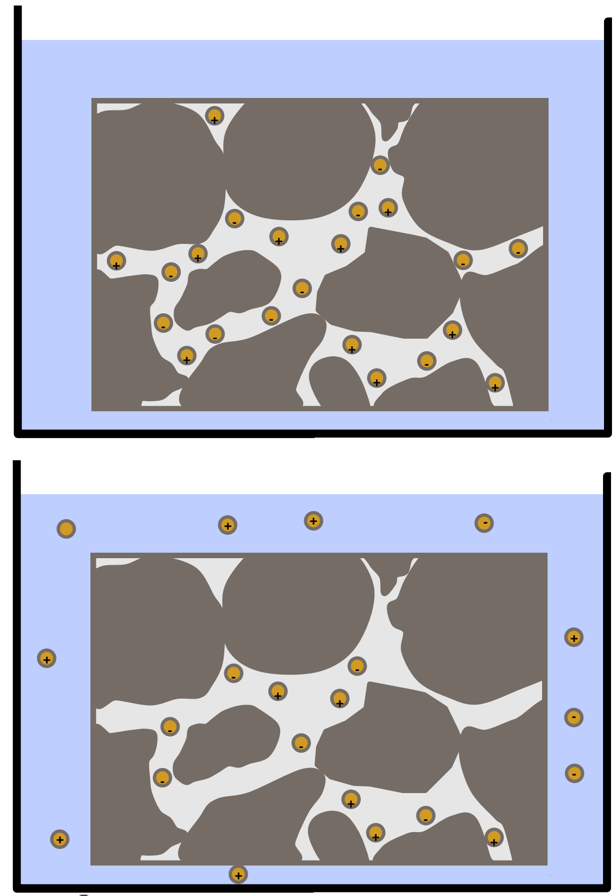

Spragg et al. 2013

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

# Leaching During Storage



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

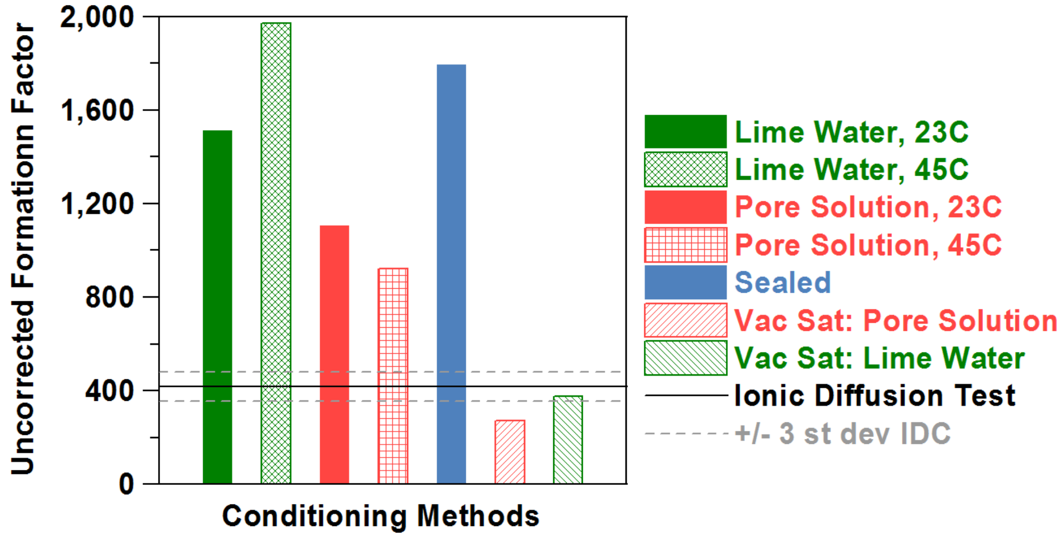


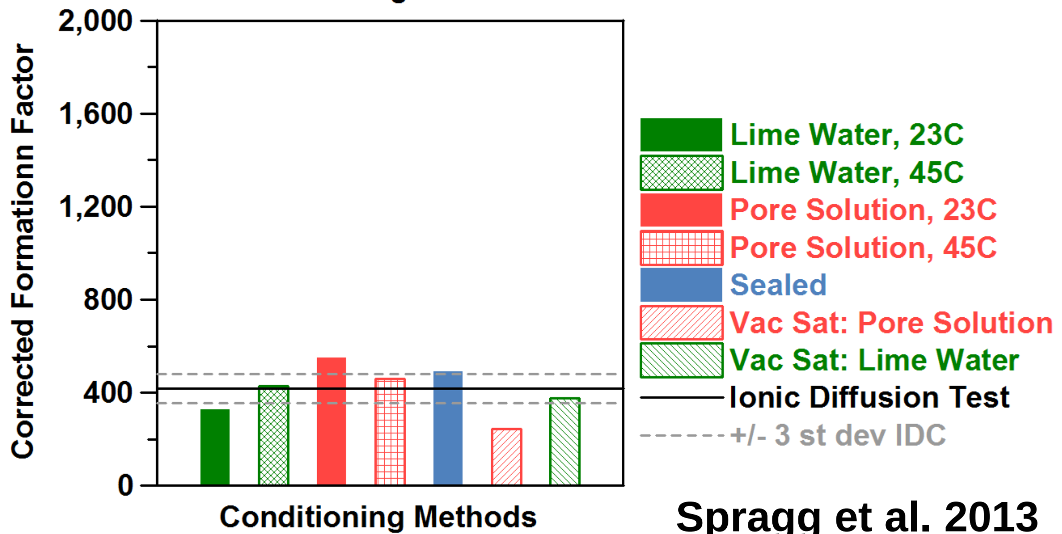
Spragg et al. 2013

# Importance of Accounting for Several Factors



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



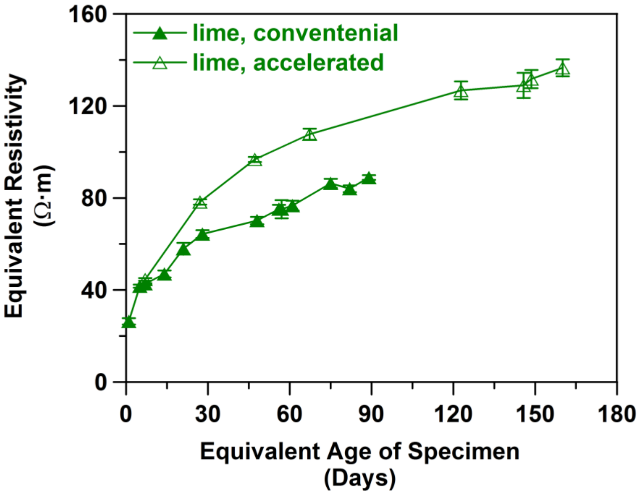




Spragg et al. 2013

# Accelerating Curing Time

Need for a New Approach
Transport Mechanisms
Pore Structure & Degree of Sat.
Gas Transport (Perm & Diff.)
Diffusion Using Fick's Second Law
Electrical Props Factors of Interest
**Accelerated Curing**
Absorption
Summary & Recommendation

- 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



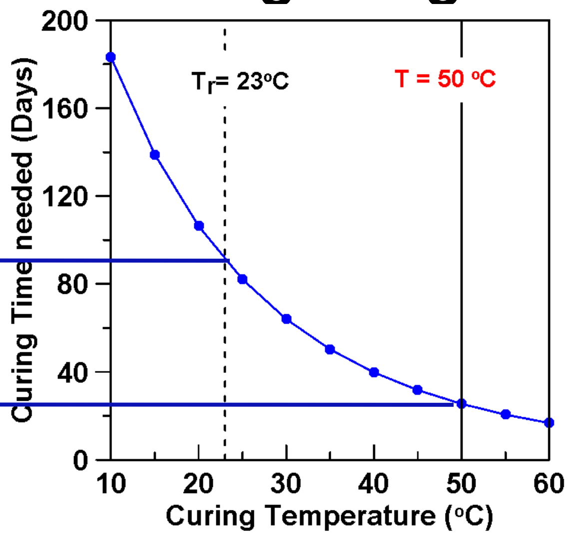
**Transport testing and service life prediction usually performed on specimens of later age (91 days).**

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

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

**91 days**

**23 days**



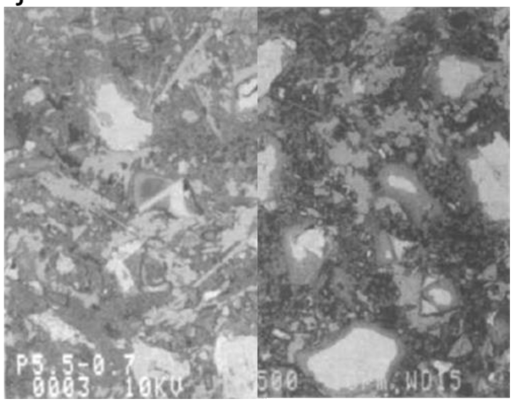

**$E_a$ = 37 kJ/mol**

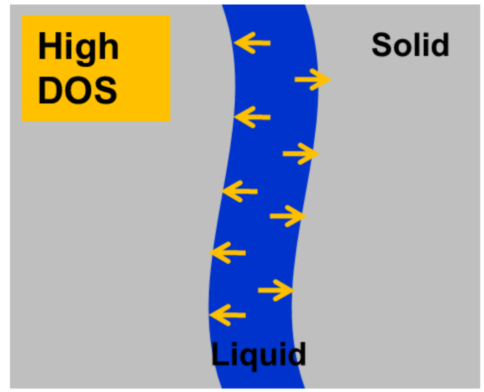
**Bu et al. 2014**

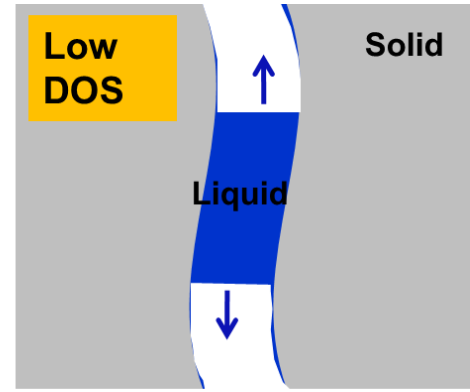
# Role of Fluid Expansion



Kjellson et al. 1990




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

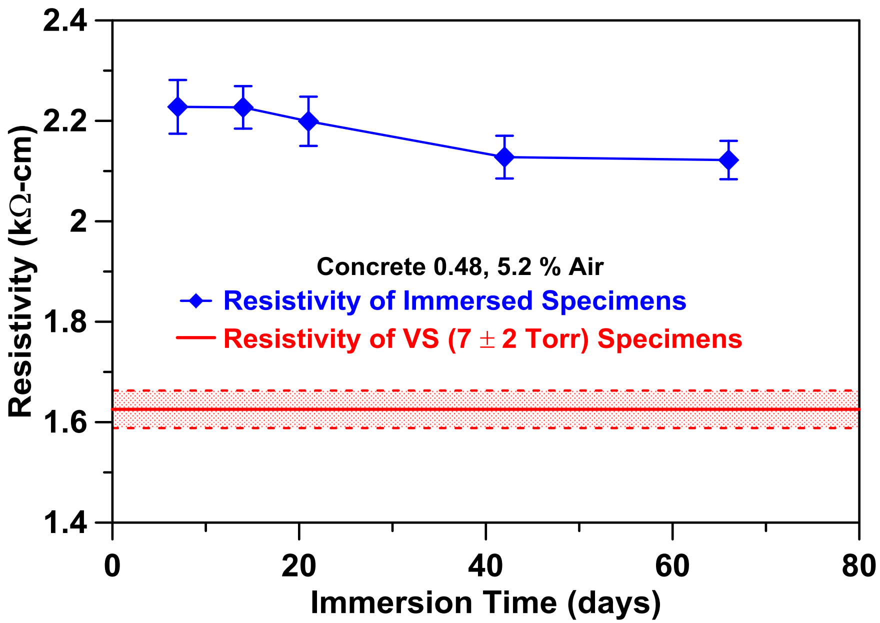
| | Porosity (%) | $D_{Cl^-}$ ($10^{-11}$ $m^2/s$) |
|---|---|---|
| NA-Wet | 16.4 | 3.66 |
| AA- Sealed | 16.3 | 3.71 |
| AA- Wet | 17.5 | 4.81 |

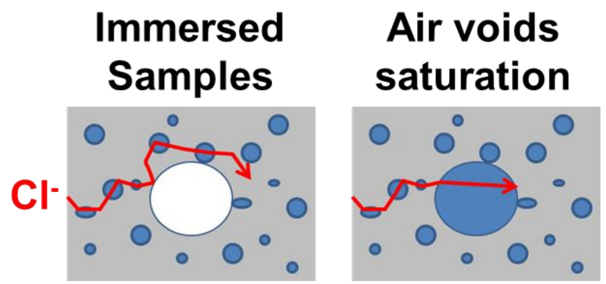
Saturated Samples 24%

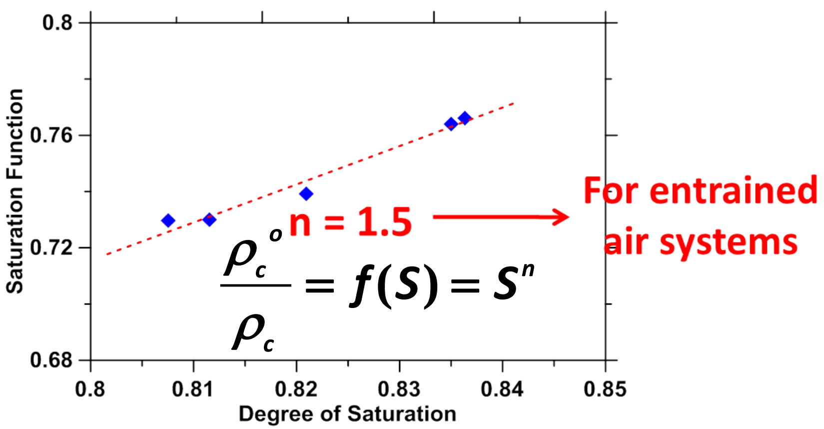
Bu et al. 2014

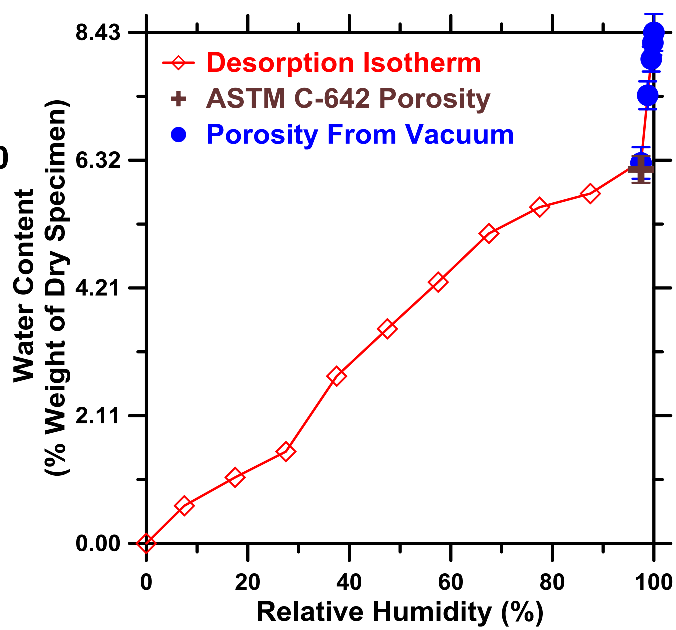
# Further Comment on Saturation





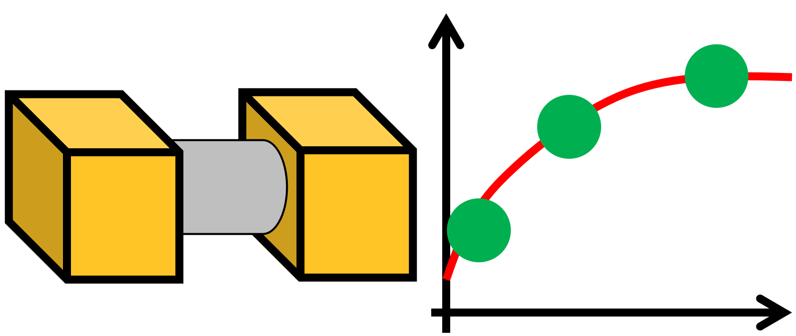

Bu et al. 2014

# Applications – Acceptance Phase



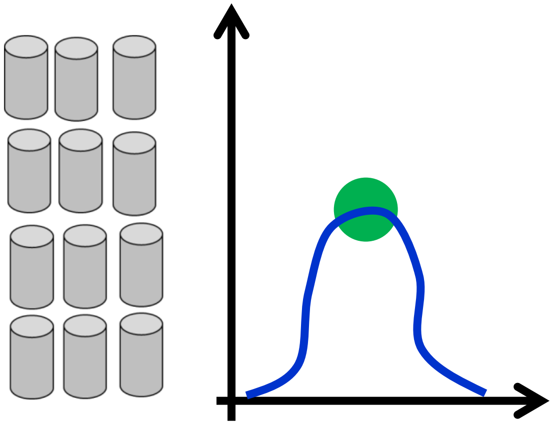
## Mixture Acceptance

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



## Quality Control

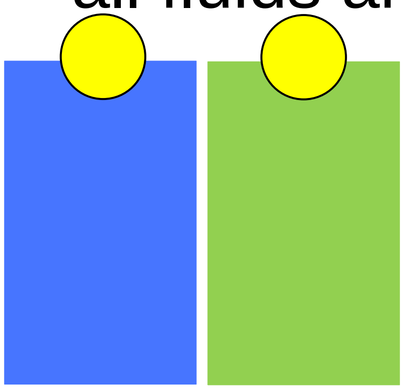
- Measurements during construction
- Test with good repeatability
- Easy tests allow for large sample size, statistical information as well



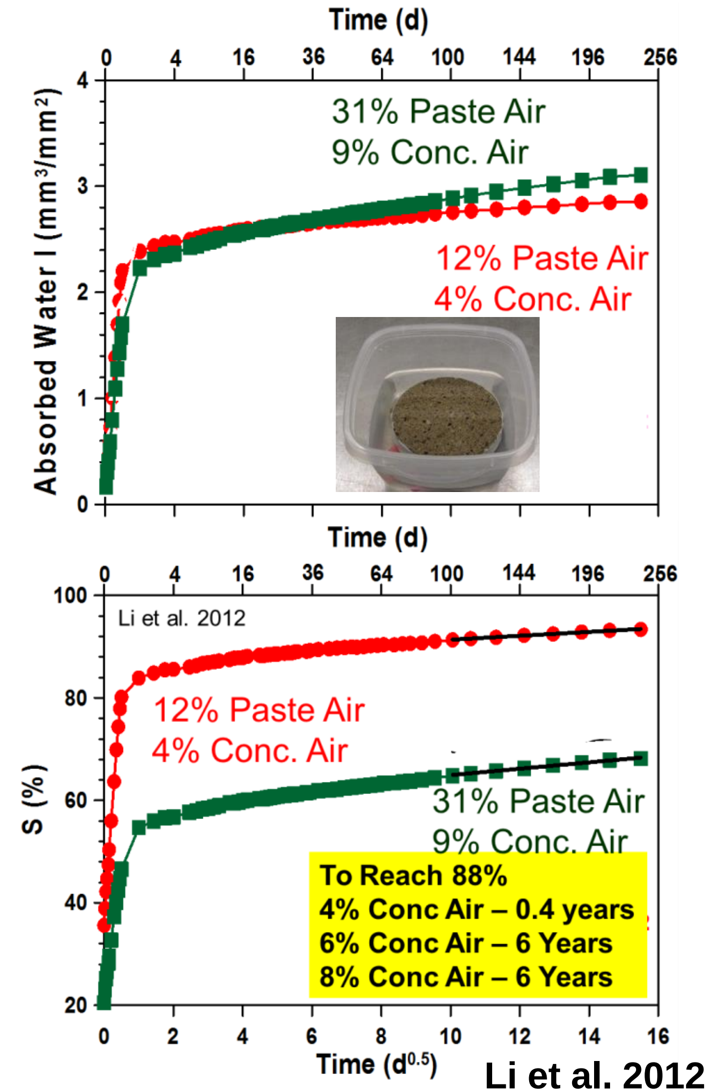
# Degree of Saturation and Air



- Mass increase like ASTM C-1585 can tell something; but
- Degree of saturation is more important (Castro et al 2012)
- Also, recall that not all fluids are water



$$x(\tau) = \sqrt{\frac{4k\,\gamma\cos(\theta)\,\tau}{\phi\,\eta\,r}}$$

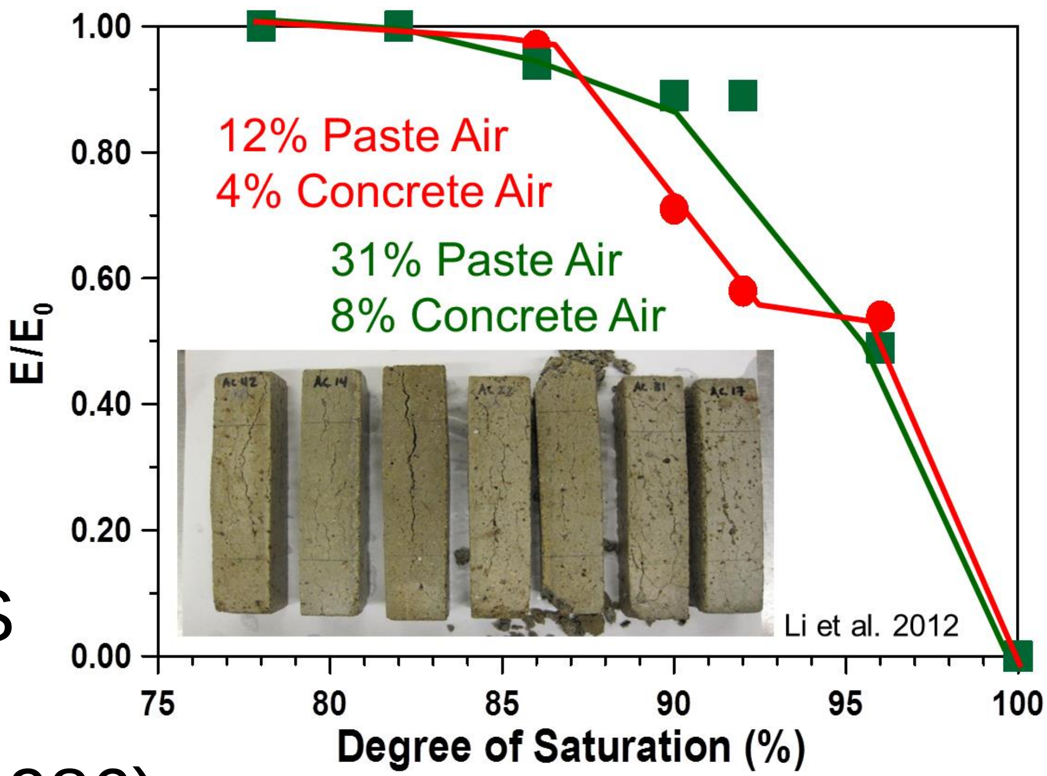



Li et al. 2012

# Degree of Saturation and Air



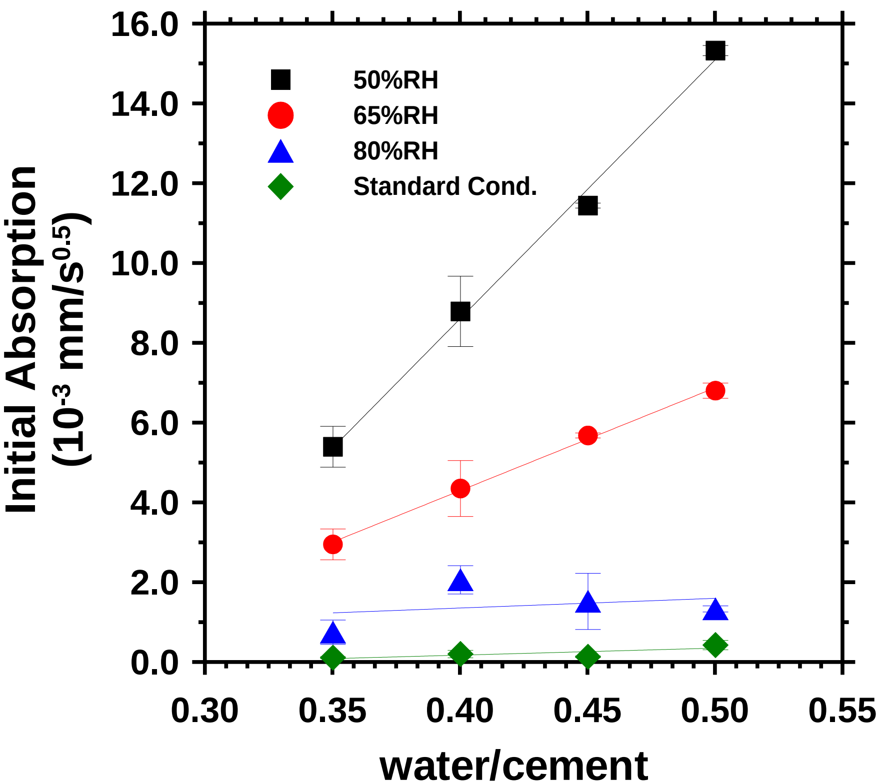
- Here we see the development of damage when the concrete has different DOS
- This is only 6 cycles
- Each cycle is a 10 to 20% decrease
- Critical DOS 86 % or so (Fagerlund1986)



# ASTM C 1585 – A Good Test with a Few Modifications



- Modification 1 - how the sample is conditioned is important, the current rapid procedure does not appear to provide a consistent point to start tests

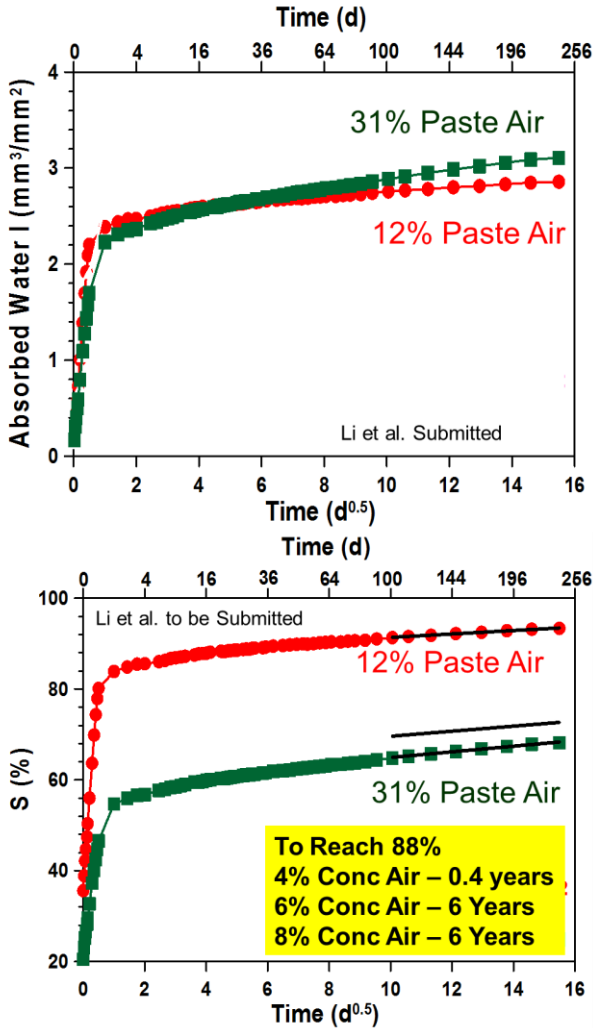



Castro et al. 2010

# ASTM C 1585 – A Good Test with a Few Modifications



- Modification 2 – the test is likely better if one considers both the rate of abs. (as currently done) and the total degree of saturation at a given time



# Summary and Recommendations - 1



- Durability can be considered using new equation/mechanism based approaches
- Permeability used but absorption, diffusion, permeation & wicking are more descriptive
- The role of sample conditioning and degree of saturation appears to be underappreciated when considering tests
  - ASTM C 642 is not a measure of total porosity
  - A DOS/vac saturation test should be considered
  - ASTM C 1585 should be DOS based
  - Many tests have confusing prep/do not match

# Summary and Recommendations - 2



- Gas Diffusion – Equation Clarified
- Gas Permeability – Equation Rederived
- Fick's Second Law (Diffusion) – $D_{APP}$ and $C_S$ depend on concentration, time, reactivity, and co-present cations
- Electrical properties
  - resistivity is a material property (geometry)
  - test temperature
  - degree of saturation
  - ionic leaching
  - curing can have major impact on variability

# Summary and Recommendations - 3



- Accelerated Curing
  - Maturity Method Can Be Applied
  - Accelerated Aging Causes Differences – Suggest Sealed Samples (low Pressure)
- Testing Confusion
  - Several Tests Performed on Saturated Samples; However Results are Compared with Partial Saturation from Lab or the Field
- Proposing Standards and Modifications
- Suggesting a Qualifying Test and a Consistency Test Be Considered


GIVE WAY
30
CYCLE LANE
LOOK BOTH WAYS
Humps for ¾ mile
RED ROUTE
No stopping at any time
GIVE WAY
LT06 LFL
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