Durability of Blended Binder Concretes Containing Limestone: Cl^- Ion Transport Experiments and Simulations

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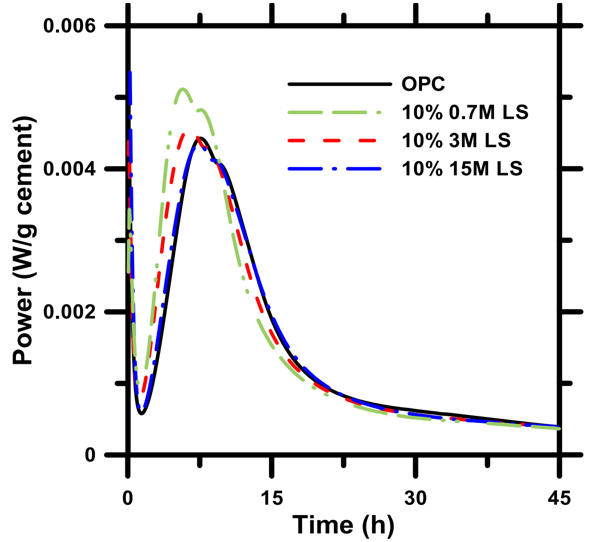
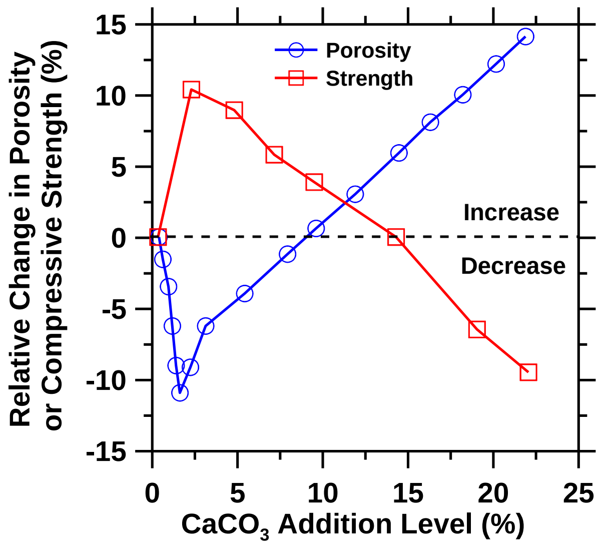
This Presentation…

- Discusses the fundamental effects of fine limestone in cementitious systems in alumina-deficient and alumina-rich conditions
- Brings out the synergistic effect of LS and MK/FA in pore structure changes that influence ionic transport
- Demonstrates the relative effects of clinker factor reduction (with LS addition as a strategy) on transport properties
- Presents a modeling strategy to predict the chloride profiles in LS-modified concrete under accelerated conditions

Limestone in Cementitious Systems

- Addition of limestone particles provides larger surface for reactions
- Higher rate of reaction, higher strength, lower porosity
- $CaCO_3$ can react with $3CaO.Al_2O_3$ (C_3A) to form CO_3^{2-}Afm phases
- In cement (with gypsum) occurs by ion-exchange to convert SO_4^{2-}AFm
- Can result in improved pore-filling and strength enhancement in system
- Very small amounts of $CaCO_3$ reactive





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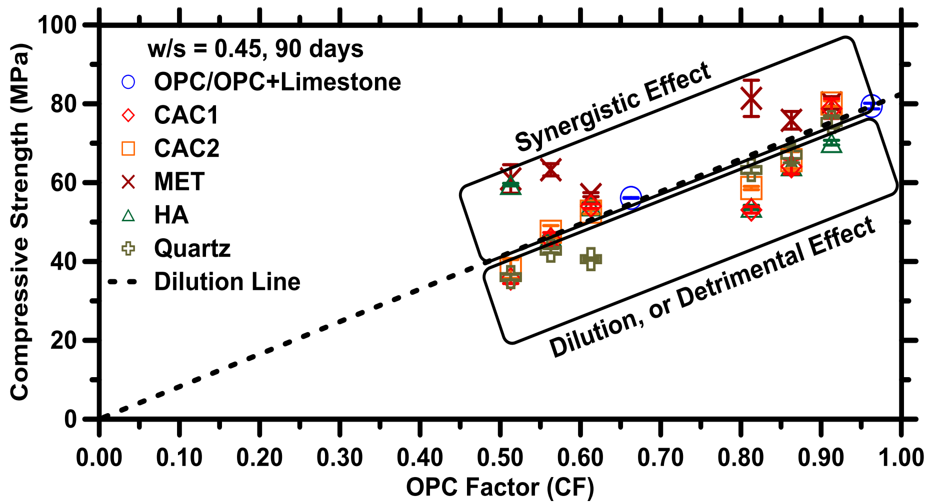
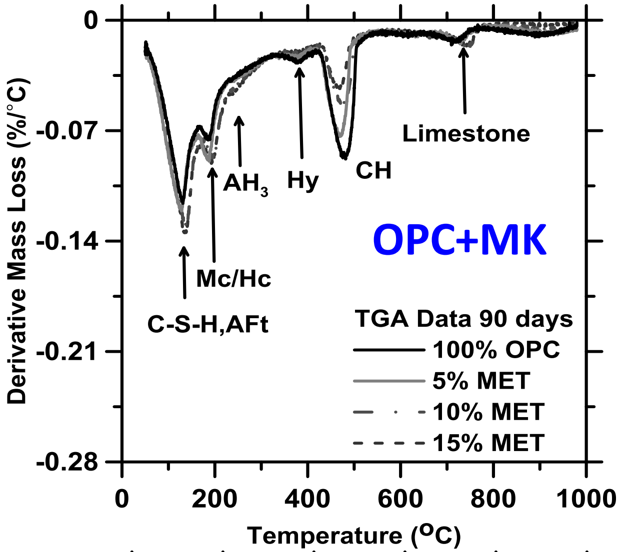
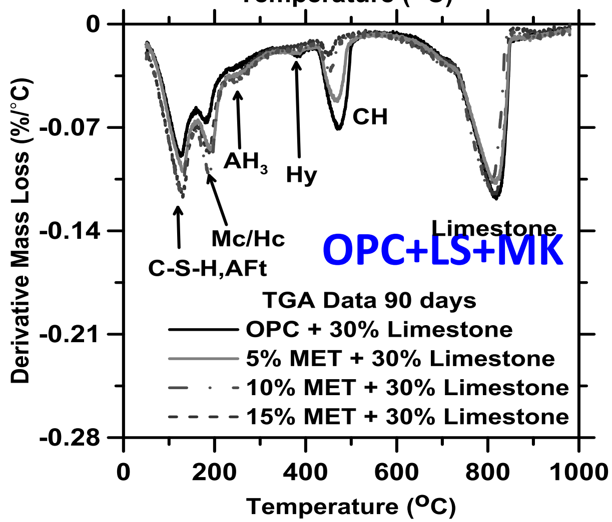
Limestone in Cementitious Systems

- Enhanced CO_3-AFm formation alone is insufficient to ensure mechanical property equivalence
- Beneficial effect of pozzolanic reaction of metakaolin or fly ash







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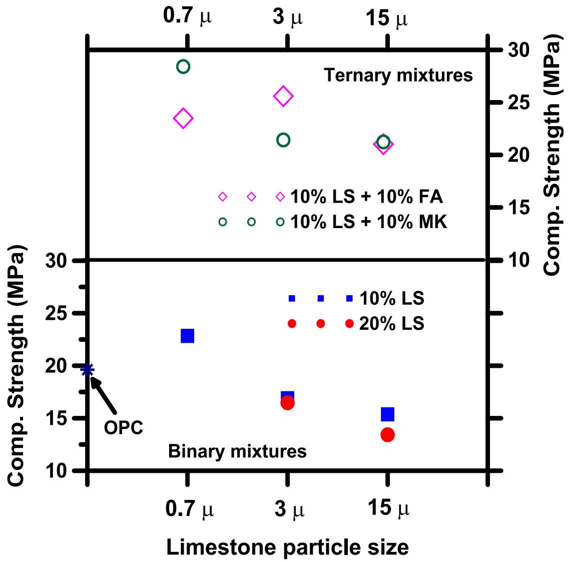
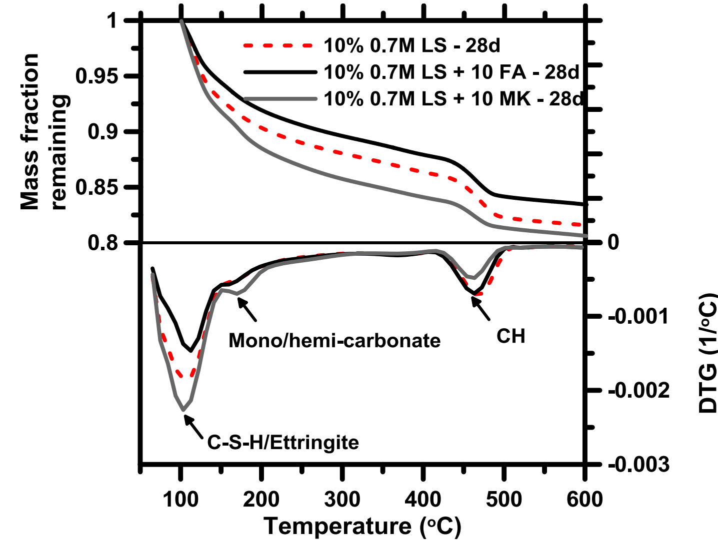
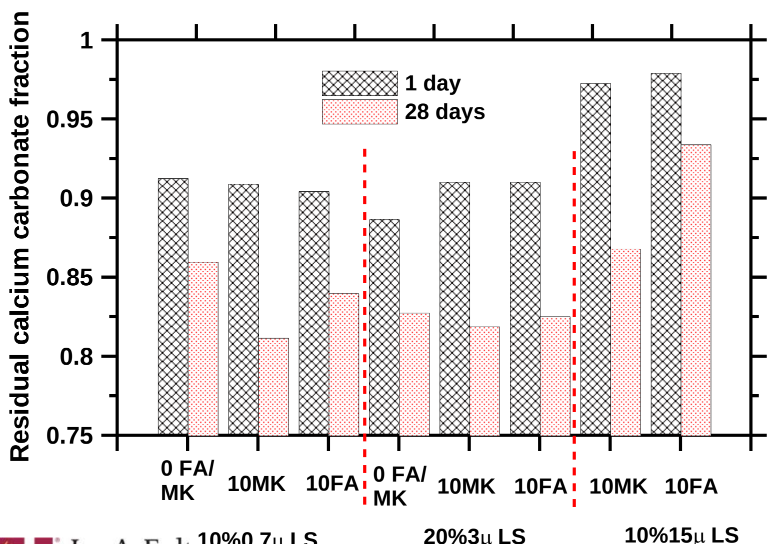
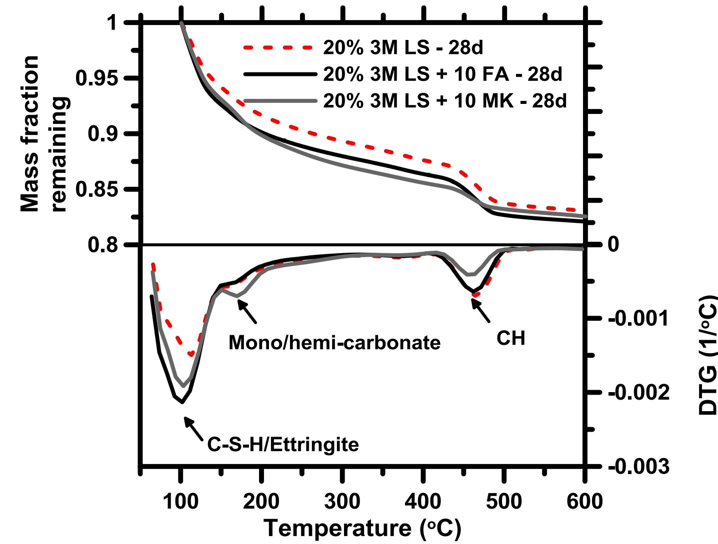
Limestone in Cementitious Systems



- Establishing pozzolanic reaction + limestone effects







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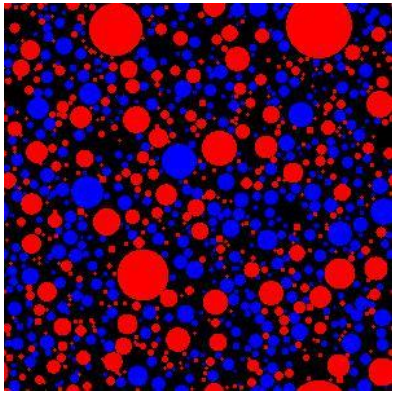
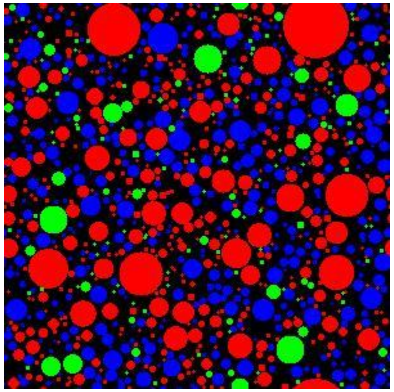
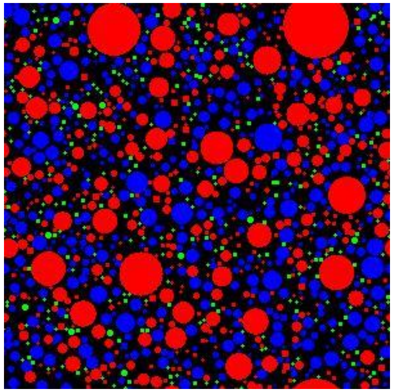
Limestone + Slag



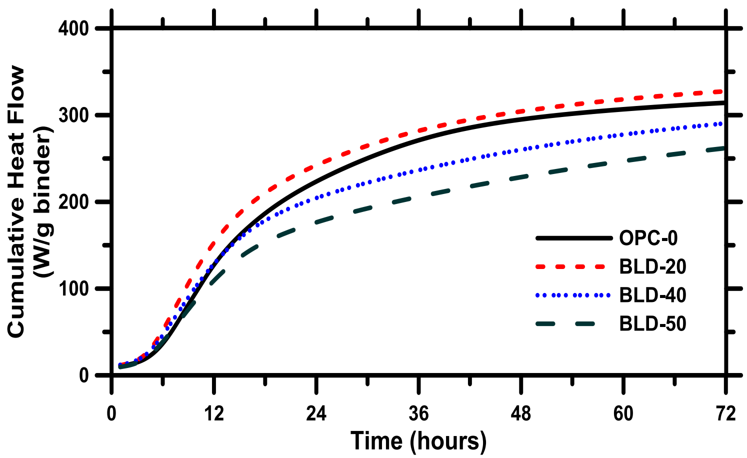
OPC + Slag (50%)

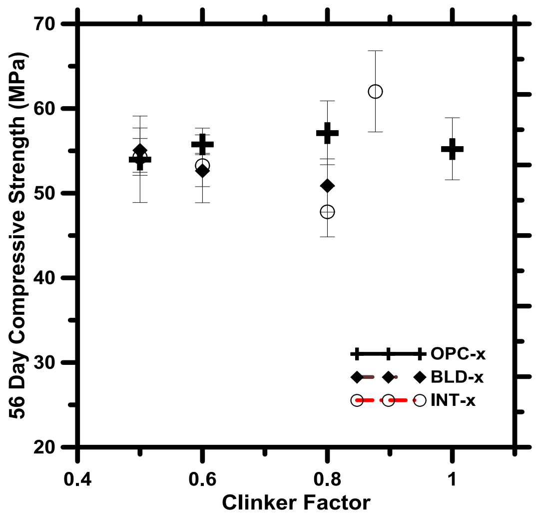


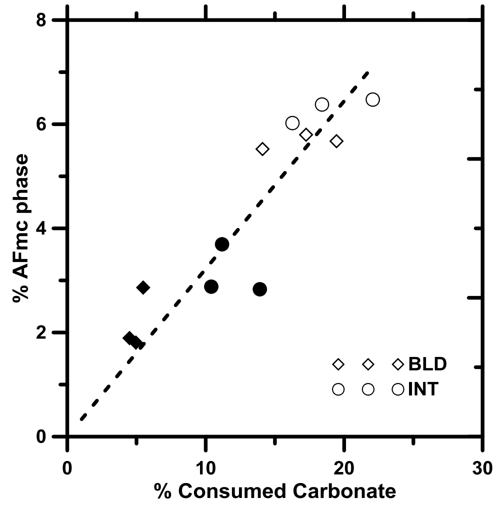
OPC + Slag (37%)
+ LS (13%)
Blended



OPC + Slag (37%)
+ LS (13%)
Interground







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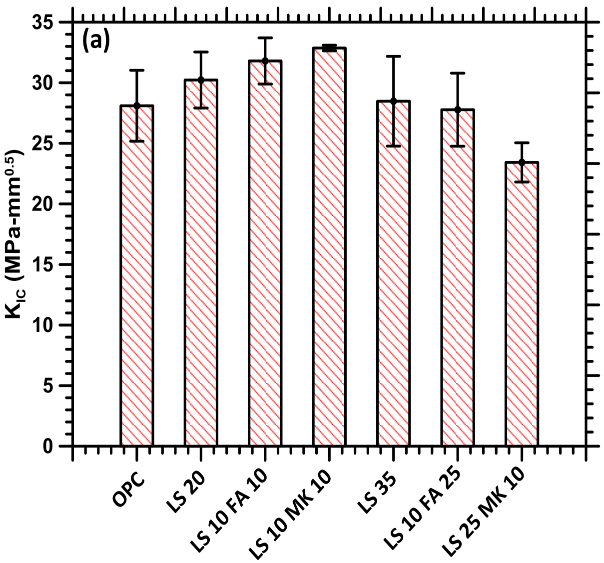
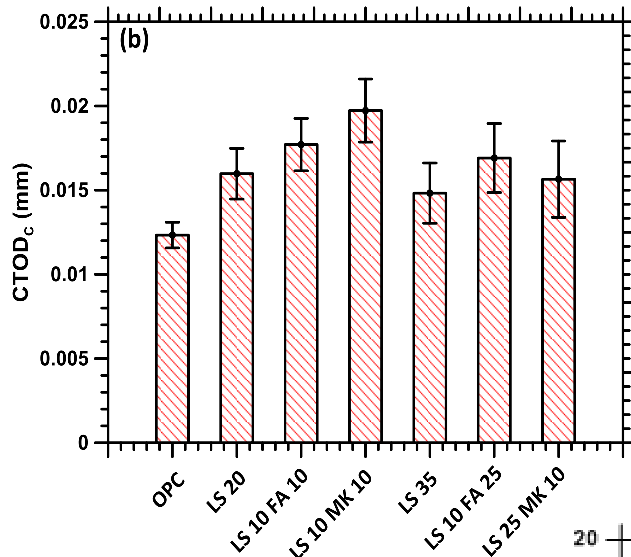
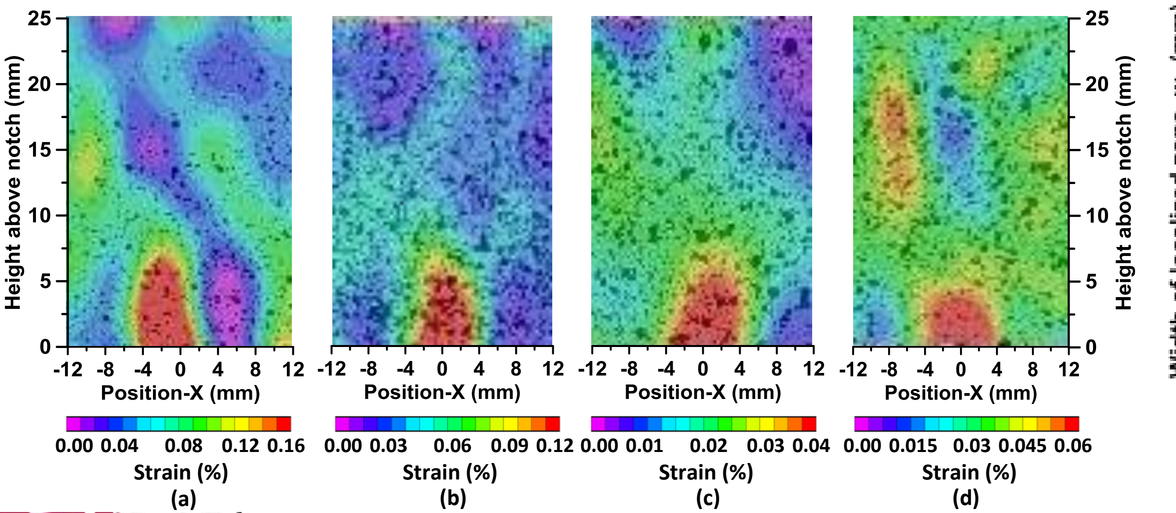
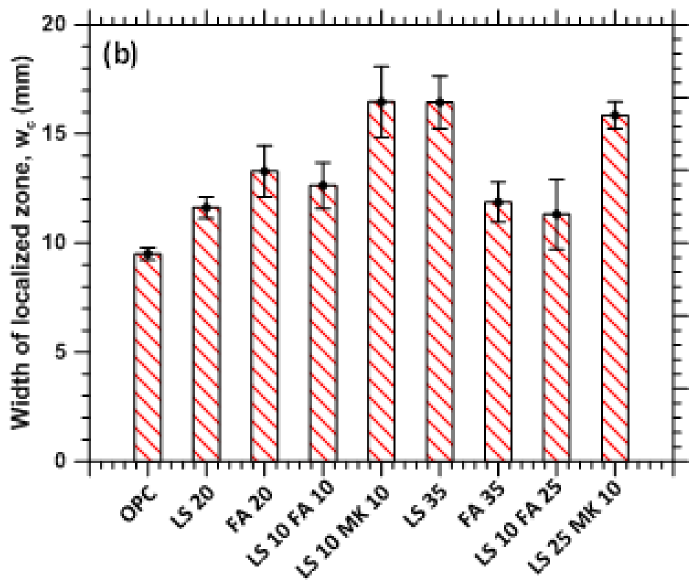
Fracture response of blended binders





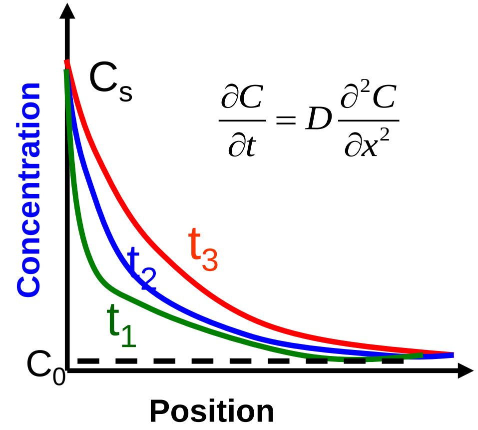
- Enhanced toughness for ternary blended binders

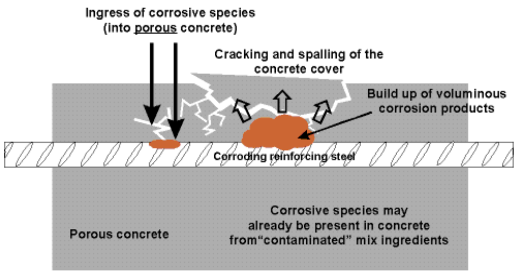




Chloride Transport

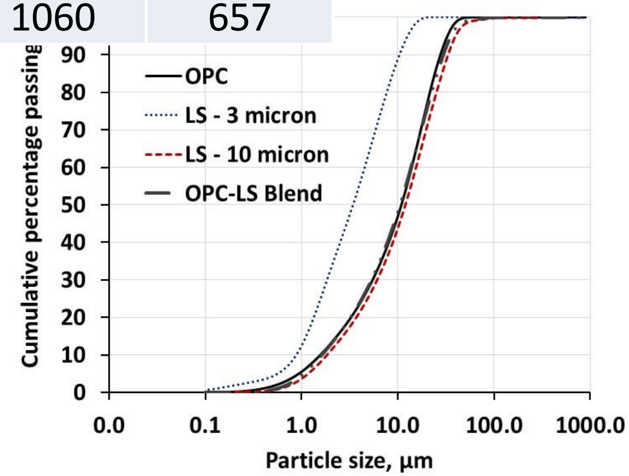
- One of the major durability predictors
- Chloride transport under an external electric field used in the development of transport testing methods
- Cations and anions move in opposite directions under an externally imposed electric field
- Transport influenced by pore structure, pore solution composition, and external electric field characteristics (test methods)



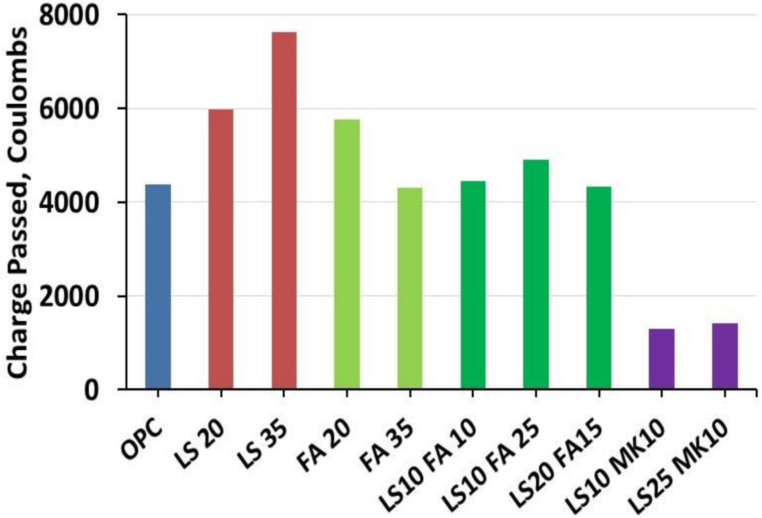


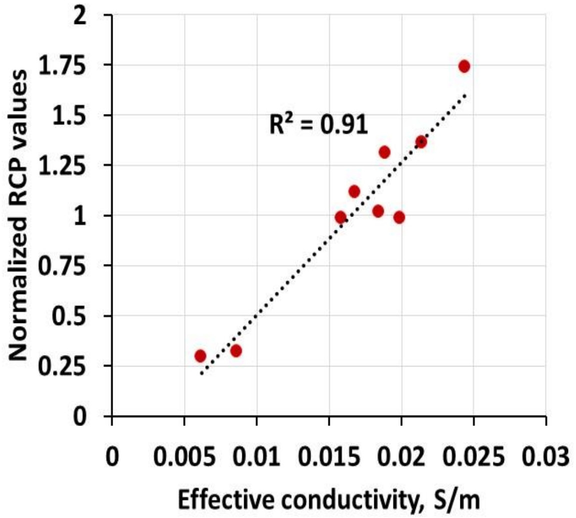
Transport in limestone modified concretes

Mixture	Cement (kg)	Limestone (kg)	Fly ash (kg)	MK (kg)	Coarse agg. (kg)	Fine agg. (kg)
Plain	480	0	0	0	1066	661
LS 20	395	85	0	0	1065	660
FA 20	399	0	80	0	1065	660
LS 10 FA 10	397	43	40	0	1065	660
LS 10 MK 10	398	43	0	38	1063	659
LS 35	327	151	0	0	1061	658
FA 35	333	0	145	0	1061	658
LS 10 FA 25	331	44	103	0	1060	657
LS 20 FA 15	330	87	61	0	1062	659
LS 25 MK 10	330	109	0	39	1060	657



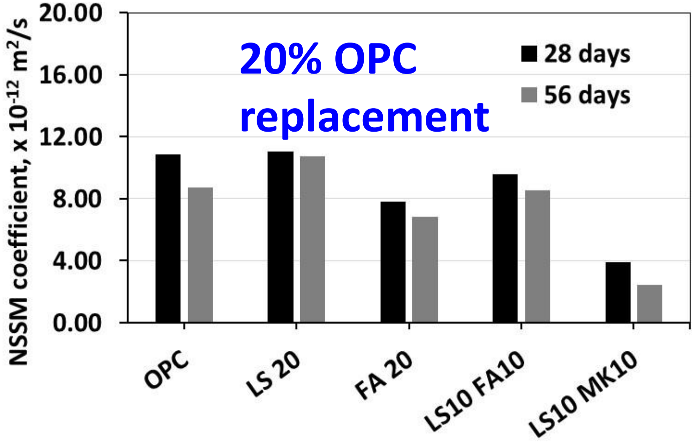
Rapid Chloride Permeability (ASTM C 1202)

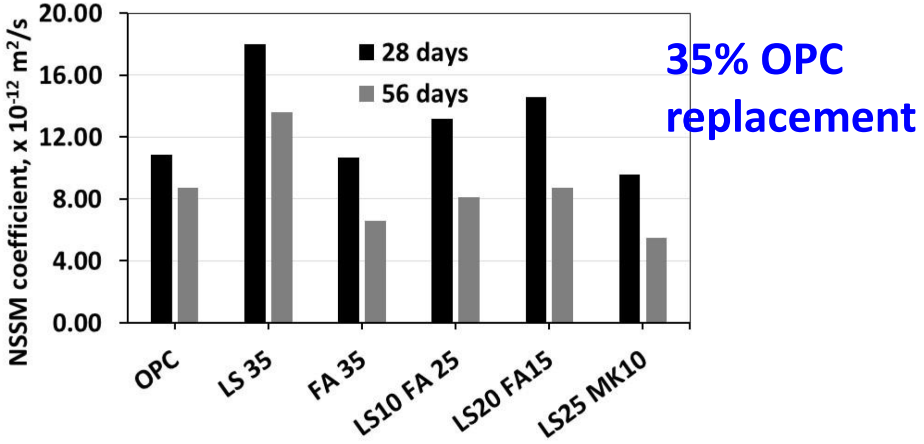




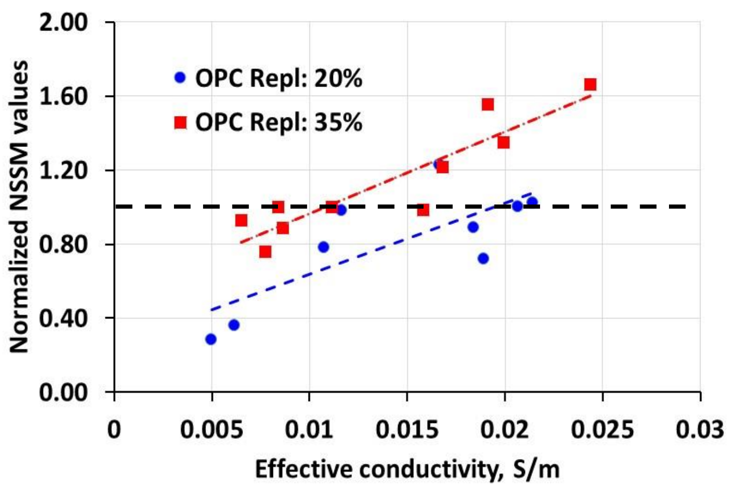
- Synergistic effects noted
- Influence of MK – pozzolanic reaction, carboaluminate formation
- Don’t discount the lower pore solution conductivity of blended binders

Non-Steady State Migration (NT Build 492)





- Indications of beneficial transport performance
- Even up to 35% total replacement without performance compromise



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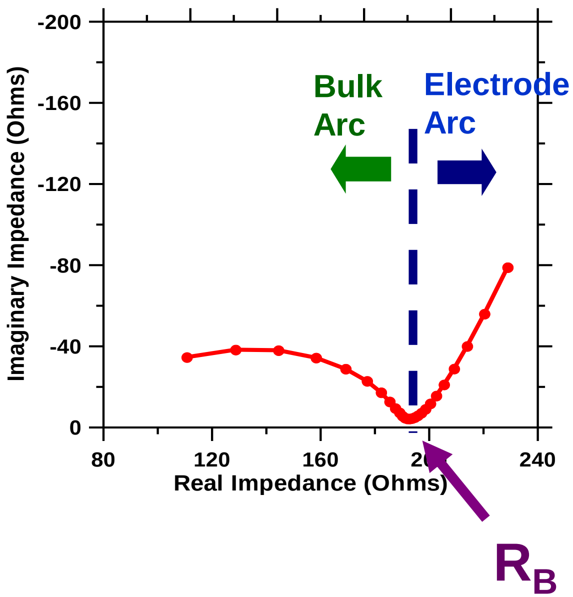
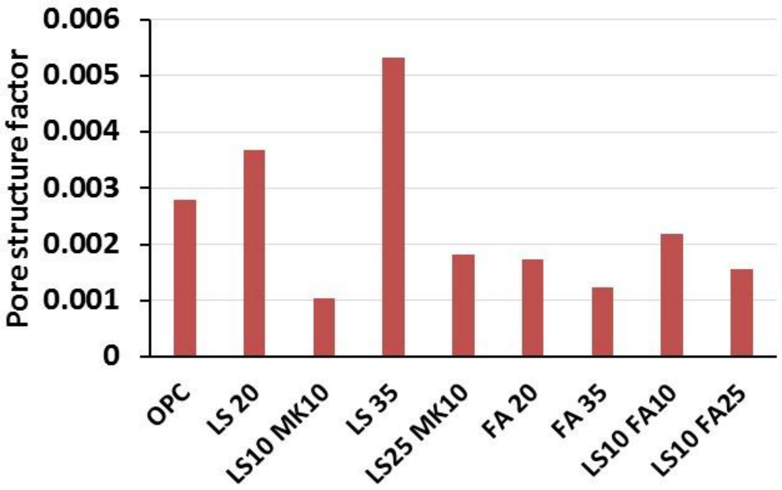
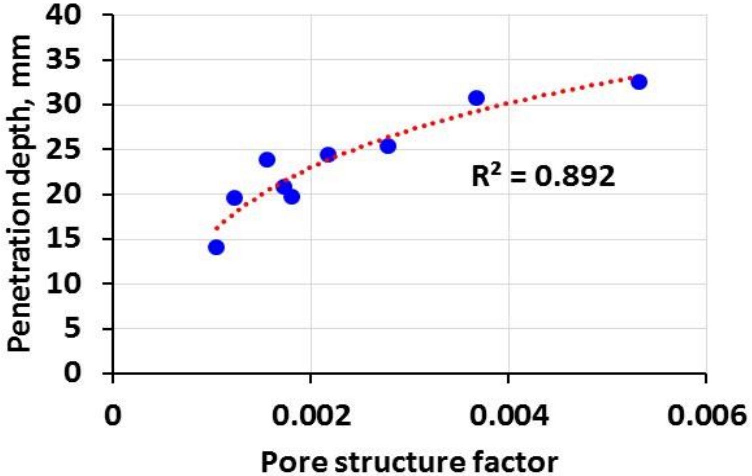
Pore Structure and Cl^- Migration

- Pore structure factor (ϕβ) from electrical impedance tests



$$\sigma_{eff} = \sigma_{pore}(\phi\beta)$$





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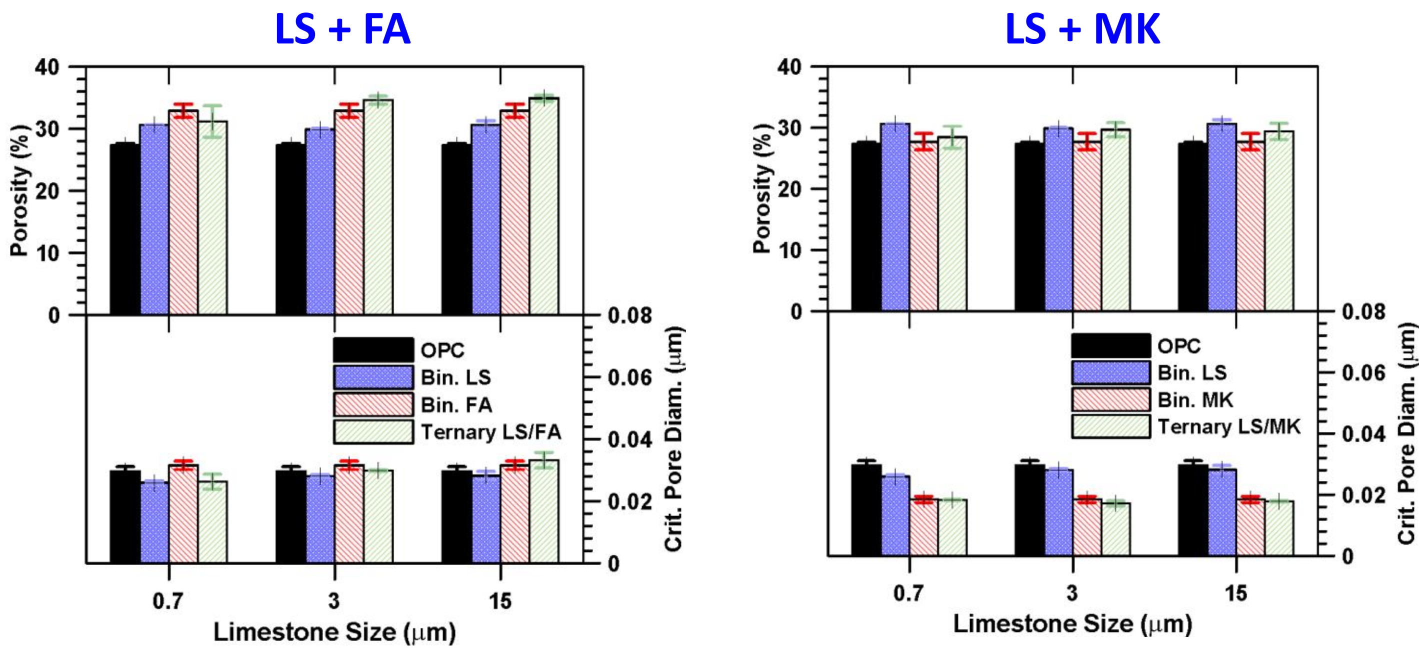
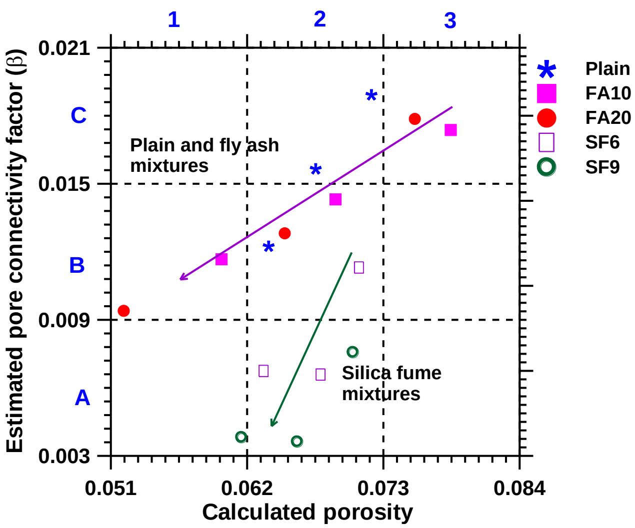
Pore structure in blended binders

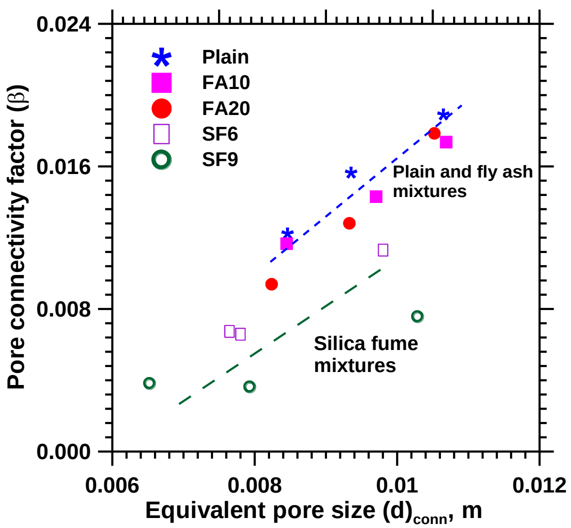


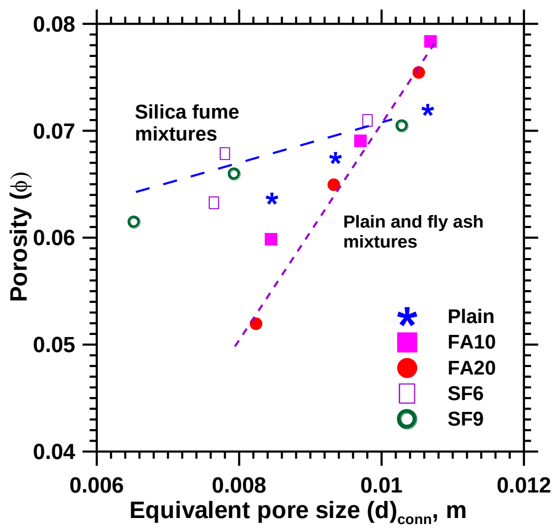
- Binary pastes – 10% OPC replacement level; Ternary pastes – 20% replacement
- 28 day porosities not very dependent on LS sizes (within range) or even the replacement level
- LS-MK ternary blends much more influential in reducing pore sizes

Pore Sizes and Transport

- Pore sizes are more influential than porosity in moisture and ionic transport
  - Pore sizes and porosity are related too…
  - Pore connectivity is a better indicator of transport
    - For a given porosity, pore connectivity is a function of the pore sizes







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Summary: Experimental Results

- Binary blends containing limestone showed higher RCP and NSSM values than the OPC (control) system, while the ternary blends containing limestone and fly ash or metakaolin showed comparable or lower RCP (and NSSM) values
- Beneficial synergy of limestone and metakaolin evident
- Pore structure factor demonstrated a strong correlation with the penetration depth of Cl^- ions.
- Pore structure factor can be used compare the transport performance of limestone blended concretes

Accurately Modeling Accelerated Transport

- Modeling ionic transport accurately depends on a proper understanding of several factors
- This results in several modeling assumptions that are needed (some less, and some more consequential)
- From a corrosion standpoint, accurate models can help develop reasonable service life predictions
  - Important to make economic decisions on repair/rehabilitation/replacement
  - Infrastructural asset management

Multi-Species Transport Modeling Gaps

- Classical Poisson-Nernst-Planck model for accelerated multi-species transport ?
- What about diffusion coefficients, electrical field distribution?
- What constitutes tortuosity in electrically accelerated ionic transport?
- How to account for binding?

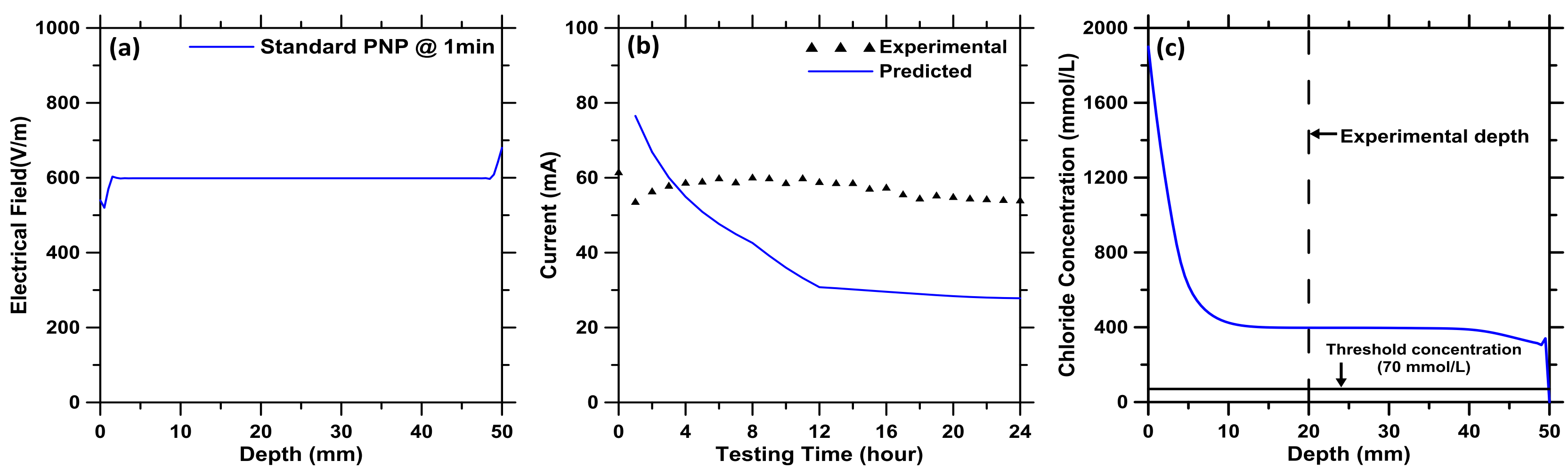
Traditional PNP model

Flux: $J_i = -D_i\left(\frac{\partial C_i}{\partial x} + \frac{z_i F}{RT} C_i \frac{\partial \Psi}{\partial x} + \frac{C_i}{\gamma_i}\frac{\partial \gamma_i}{\partial x}\right) - C_i v(x)$

Mass conservation: $\frac{\partial(\phi C_i)}{\partial t} = -div(J_i)$

Poisson equation: $\nabla^2 \Psi = -\frac{F}{\varepsilon_0 \varepsilon_r}\sum_i C_i z_i$

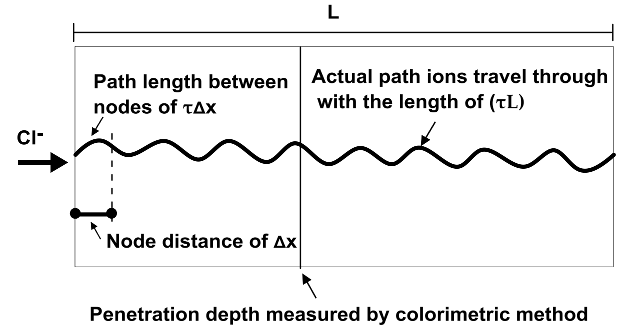
Effective diffusion coefficient: $D_i^{eff} = \frac{\phi}{\tau^2} D_i = \phi\beta D_i$



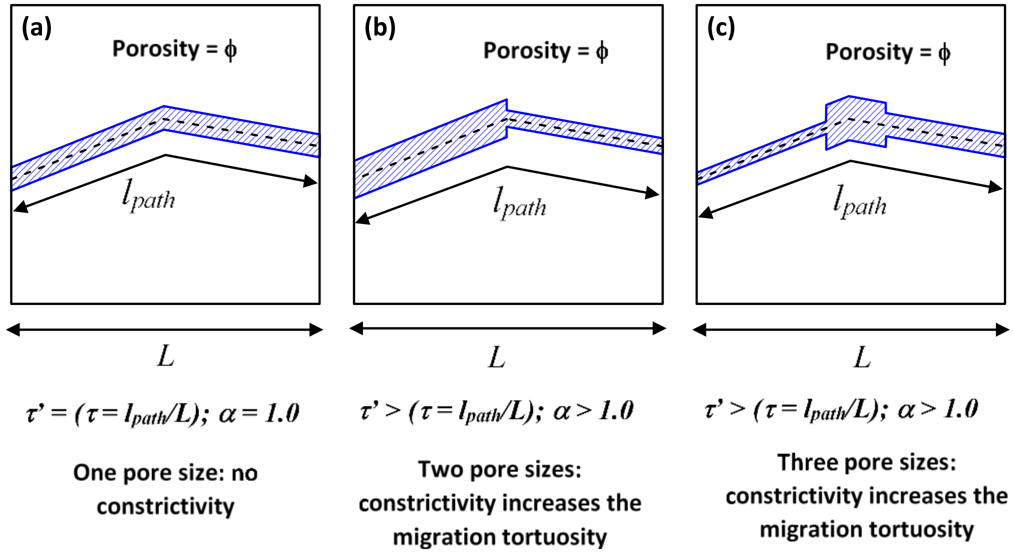
Rational Modifications

$$\frac{\partial(\phi C_i)}{\partial t} = \phi D_i \frac{\partial}{\partial(\tau x)}\left[\left(\frac{\partial C_i}{\partial(\tau x)}\right) + \frac{z_i F}{RT}\left(C_i \frac{\partial \Psi}{\partial(\tau x)}\right)\right]$$

$$D_i = \frac{\lambda_i}{\lambda_i^0} D_i^{inf}$$

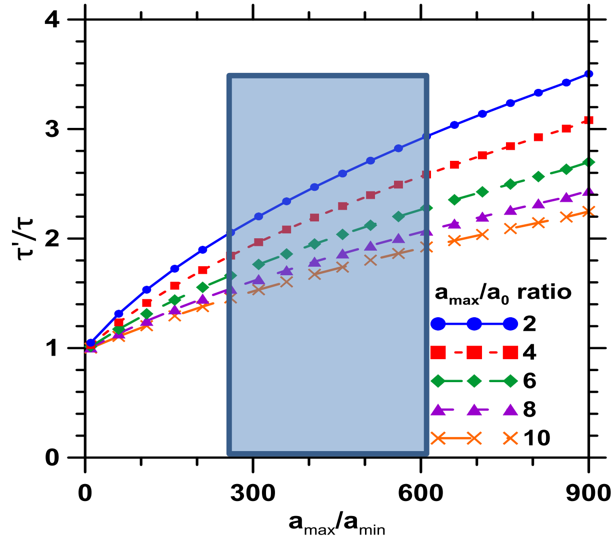


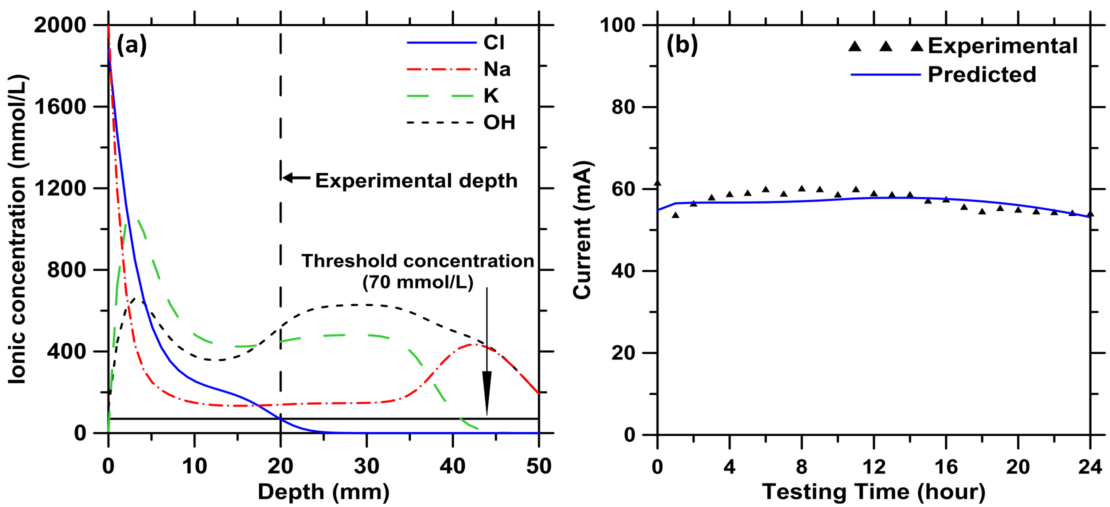
- Introducing changes in the way tortuosity is considered
- Electrically measured tortuosity is not equivalent to the geometric tortuosity
  - Electrical streamlines do not follow the centerline of the pore path.

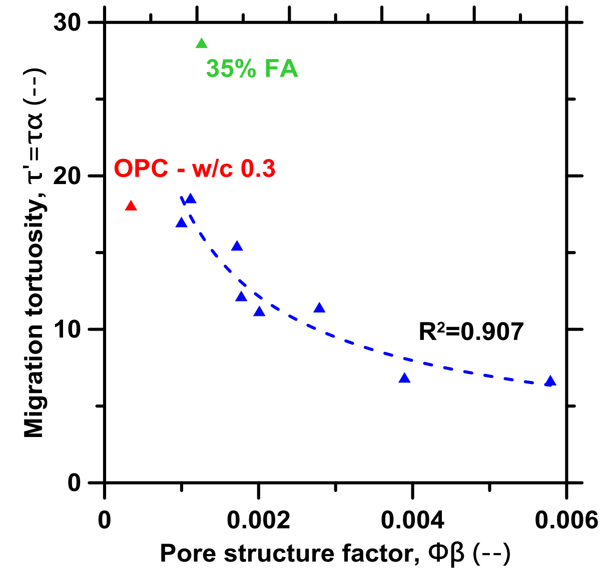


Rational Modifications

- Relationship between geometric and electrical tortuosities explained by pore area ratios - MIP data useful
- For many cementitious systems containing maximum-to-minimum pore size ratios in the range of 15 to 25 (pore area ratios in the range of 225 to 625), the correction factors for tortuosity vary between 1.5 and 2.5







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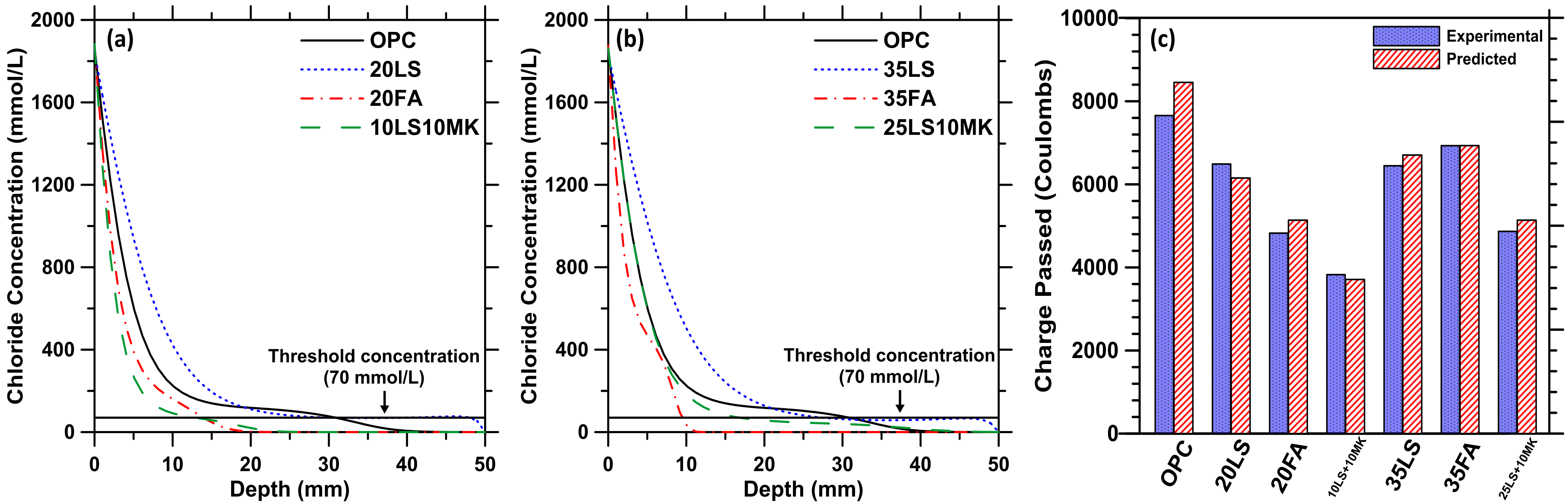
Reactive Considerations

- Reactions under electrically induced movement – subject of debate
- Prediction based on the Freundlich isotherm being obeyed at each time step in the calculation:

$$C_b^n = k_b\left(C_f^n\right)^m$$

- $\frac{\partial(\phi C_f)}{\partial t} + \frac{\partial((1-\phi)\rho_{dry} C_b)}{\partial t} = \phi D_{Cl} \frac{\partial}{\partial x}\left(\frac{\partial C_f}{\partial x}\right) + \phi D_{Cl} \frac{z_i F}{RT} \frac{\partial}{\partial(\tau' x)}\left(C_i \frac{\partial \Psi}{\partial(\tau' x)}\right)$
- More refinement needed to account for changes in rate of binding

Model Validations



- Influence of replacement materials that function as reactive materials or fillers noticed from the penetration profiles and the depth, due to their contribution to the pore structure
- Satisfactory prediction of charge passed that the standard PNP model is incapable of

Summary

- Carboaluminate formation favored in the presence of reactive alumina-bearing species, along with the impact of the pozzolanic reaction
- Ternary blends containing MK or FA beneficial with LS (Clinker factors up to ~0.6), while slag and LS blends are beneficial at even lower (~0.5) clinker factors
- Transport performance and its dependence on the pore structure brought out
- A modified version of the PNP model helps predict the transport characteristics accurately
- Modeling approaches need to be sufficiently integrated with experiments for service life prediction

Thank You….

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