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$_2$O$_3$ (C$_3$A) 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
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.
• Establishing pozzolanic reaction + limestone effects
Limestone + Slag

OPC + Slag (50%)  
OPC + Slag (37%) + LS (13%)  
OPC + Slag (37%) + LS (13%)  
Blended  
Interground

Graphs showing the cumulative heat flow, 56-day compressive strength, and % A-fm phase over time and clinker factor. The graphs compare OPC and blended materials with different slag contents.

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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

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Cement (kg)</th>
<th>Limestone (kg)</th>
<th>Fly ash (kg)</th>
<th>MK (kg)</th>
<th>Coarse agg. (kg)</th>
<th>Fine agg. (kg)</th>
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<tr>
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<td>39</td>
<td>1060</td>
<td>657</td>
</tr>
</tbody>
</table>

![Cumulative percentage passing](chart.png)
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
Pore Structure and Cl⁻ Migration

- Pore structure factor (\(\phi\beta\)) from electrical impedance tests

\[
\sigma_{\text{eff}} = \sigma_{\text{pore}}(\phi\beta)
\]

![Graph showing pore structure factor and penetration depth](image-url)
• 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
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?
Flux: \( J_i = -D_i \left( \frac{\partial C_i}{\partial x} + \frac{z_i F}{RT} C_i \frac{\partial \Psi}{\partial x} + \frac{C_i \partial y_i}{\gamma_i \partial x} \right) - C_i \nu(x) \)

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

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

Effective diffusion coefficient: \( D_i^{\text{eff}} = \frac{\phi}{\tau^2} D_i = \phi \beta D_i \)
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.

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

\[
D_i = \frac{\lambda_i}{\lambda_i^0} D_{inf}
\]

Rational Modifications:

(a) Porosity \(= \phi \)
(b) Porosity \(= \phi \)
(c) Porosity \(= \phi \)

Path length between nodes of \(\tau \Delta x\) Actual path ions travel through with the length of \((\tau L)\)

Penetration depth measured by colorimetric method

\(\tau' = (\tau = \frac{l_{path}}{L}); \quad \alpha = 1.0\)

One pore size: no constrictivity

\(\tau' > (\tau = \frac{l_{path}}{L}); \quad \alpha > 1.0\)

Two pore sizes: constrictivity increases the migration tortuosity

\(\tau' > (\tau = \frac{l_{path}}{L}); \quad \alpha > 1.0\)

Three pore sizes: constrictivity increases the migration tortuosity
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
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:
  \[ C_b^n = k_b (C_f^n)^m \]
  \[
  \frac{\partial (\phi C_f)}{\partial t} + \frac{\partial ((1-\phi) \rho_{dry} C_b)}{\partial t} = \phi D_{Cl} \frac{\partial}{\partial x} \left( \frac{\partial C_f}{\partial x} \right) + \phi D_{Cl} \frac{z_i F}{RT} \frac{\partial}{\partial (\tau' x)} \left( C_i \frac{\partial \Psi}{\partial (\tau' x)} \right)
  \]
- 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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