Experimental investigation on evolution of pore structure by different techniques

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Outline of the presentation

» Background

» Objectives and scope of the study

» Characterization of the cement (LC³ – IITM)

» Results from different techniques
  » Mercury intrusion porosimetry
  » Electrical impedance spectroscopy

» Discussion

» Concluding remarks
Why porosity characterization?

- Mechanical property
  - Strength
  - Permeability
  - Shrinkage

- Physical property
  - Shrinkage
  - Creep

Capillary porosity
- 10μm – 10 nm

Gel porosity
- 10 nm – 0.5 nm

Interlayer spaces
- < 0.5 nm

Micro-crack and ITZ
- 20 μm – millimeters

- Within hydrate phases
- Strength
- Permeability

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http://iti.northwestern.edu/cement/monograph/Monograph7_2.html
Objectives and scope of the study

» Primary objective is to compare the porosity and pore size distribution for pastes with limestone calcined clay (LC3) cement, and compared with OPC and fly ash – cement paste

» Additionally, the study aims to compare the porosity estimates from MIP and other techniques

» Scope
  » Binder types: OPC, 70% OPC + 30% Class F fly ash, and Trial Blend of LC3
  » Tests: Mercury Intrusion Porosimetry (MIP) and Electrical Impedance Spectroscopy (EIS)
Cementitious blends used

» Ordinary portland cement - OPC
» 70% OPC + 30% fly ash - FA30
» Limestone and calcined clay cement (55% OPC + 30% Calcined clay + 15% Limestone) – LC³ – IITM
» Paste with w/b of 0.35
Cement characterization

Physical characteristics | LC³ - IITM
---|---
Specific gravity | 2.96
Consistency | 37%
Initial setting time | 145 min
Final setting time | 270 min
28 day strength (MPa) | 39.6

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Mercury Intrusion porosimetry
Mercury Intrusion porosimetry (MIP)

» Intrusion of mercury under controlled pressure

» Washburn equation: connects Pressure to the pore entry diameter corresponding

\[ P = \frac{4 \gamma \cos \theta}{d} \]

Mercury intrusion porosimeter facility, IITM Pascal 140 and 440 series
Pore structure evolution of OPC

Variation of cumulative pore volume Vs pore diameter over age (OPC)

Not much refinement in the threshold diameter from 7 to 28 days

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Pore structure evolution of FA30

Variation of cumulative pore volume Vs pore diameter over age (FA30)

Pozzolanic reaction starts refinement of the capillaries by 28 days

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Pore structure evolution of LC³

Variation of cumulative pore volume Vs pore diameter over age (LC³ - IITM)

Refinement of capillary pores seen from as early as 3 days

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Refinement of pore structure in LC³

- Highly refined pore structure early up.
- Overall intrusion seems to be higher, but pore sizes are shifted.
- Fly ash blend similar to LC3 at 28 days.

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Results from MIP

### Most likely diameter (μm)

<table>
<thead>
<tr>
<th>Age (days)</th>
<th>OPC</th>
<th>FA30</th>
<th>LC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 day</td>
<td>0.365</td>
<td>0.373</td>
<td>0.051</td>
</tr>
<tr>
<td>7 day</td>
<td>0.080</td>
<td>0.122</td>
<td>0.015</td>
</tr>
<tr>
<td>28 day</td>
<td>0.041</td>
<td>0.019</td>
<td>0.013</td>
</tr>
</tbody>
</table>

### Threshold diameter (μm)

<table>
<thead>
<tr>
<th>Age (days)</th>
<th>OPC</th>
<th>FA30</th>
<th>LC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 day</td>
<td>1.526</td>
<td>1.078</td>
<td>0.126</td>
</tr>
<tr>
<td>7 day</td>
<td>0.204</td>
<td>0.203</td>
<td>0.056</td>
</tr>
<tr>
<td>28 day</td>
<td>0.062</td>
<td>0.052</td>
<td>0.036</td>
</tr>
</tbody>
</table>

- Lower threshold in LC3 $\Rightarrow$ more difficult to penetrate by aggressive agents
- Overall pore refinement 3 times better than OPC
Electrical Impedance Spectroscopy
Electrical Impedance spectroscopy

**Test parameters:**

- Frequency range: 0.1 Hz to 10 MHz
- Amplitude: 250 mV
- Measured at 100% RH
Typical Nyquist plots at 28 days

- Higher resistance in LC³ system
Lower conductivity in LC\textsuperscript{3} due to early refinement of microstructure

- Modified Archie's Law
  \[ \sigma_{eff} = \sigma_p \phi_p^m + \sigma_s \phi_s^m \]

- Porosity can be estimated from the electrical response

Sanish et al. (2013)
Porosity evolution from AC Impedance spectroscopy

- Refined microstructure from early age in LC3 – Early strength gain is due to this refined porosity in the system.

- Pozzolanic reaction from Fly ash has prominent effect on microstructure only beyond 14 days in FA30.
Discussion – differences in hydration kinetics

- High dissolution of CH from early stage
- Additional hydrates such as Mc
- Stabilization of early Ettringite

Matschei et al. (2007), Lothenbach et al. (2008)
Concluding Remarks

» Microstructural characterization with respect to Pore structure and Porosity is essential to understand the performance of the blended system

» Study of pore structure evolution over time helps understand hydration kinetics of the LC³

» Ternary blend containing Limestone and calcined clay shows more refined pore structure compared to fly ash blend and OPC, as early as 3 days

» Results from both MIP and EIS suggest better performance of LC3 blends at early ages; in the long term, the fly ash blend improves with respect to pore structure, thanks to the late pozzolanic activity of fly ash...
Thank You for your attention

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