Controlling Microcracking in Low Embodied Energy Concrete

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SOME FACTS ABOUT CEMENT

Clinker: $3\text{CaO}\cdot\text{SiO}_2$

$\text{CO}_2$ sources:
- Chemistry $\sim 55\%$
  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
- Fuel $\sim 45\%$

Total $\sim 0.8$ t / t clinker
SOME FACTS ABOUT CEMENT

THE HIDDEN DETAILS

- Cement manufacture makes up 5-8% of all CO₂
- Second most used material next to WATER
- ~ 0.8-0.9 ton of CO₂ per 1 ton of cement
- Market to double by 2050

Alternatives to ordinary Portland cement (OPC) are required to meet the VAST MAJORITY of cement in concrete.
ALKALI-ACTIVATED CONCRETE (GEOPOLYMERS)

Metallurgical Slags

Fly Ash

Natural Pozzolans

Alkaline Activator

Cementitious Components

Binder for Concrete
COMMERCIALIZATION OF ALKALI-ACTIVATED CONCRETE

• Late 1950s - Glukhovsky in Kiev developed alkali activated binders, followed by Krivenko, who constructed slag AAC structures and a high rise building in Russia in the 1960s.

• Davidovits coined term geopolymer in the 1970s.

• Today many universities research alkali-activated concrete (geopolymers), but still little commercial activity.
  • Specific research-related road blocks
RESEARCH ON ALKALI-ACTIVATED MATERIALS

Nanostructural Ordering: Synchrotron Diffraction

Gel Pores: Neutron Small-Angle Scattering

In situ Carbonation: Synchrotron Diffraction

Microcracking: Image Analysis

Permeability: Beam-Bending Technique

White et al., Cement and Concrete Research, 2015.
SUSCEPTABILITY TO MICROCRACKING

• Certain mix designs of alkali-activated pastes are prone to crack
  – Known as *microcracking*
  – Different form of cracking compared to cracks induced due to loading (tension in reinforced concrete)
  – Microcracking increases susceptibility to chemical degradation

Cracking in reinforced concrete due to bending

Microcracking in alkali-activated slag paste

Sumajouw and Rangan, 2006
CAUSE(S) OF MICROCRACKING

• Microcracking is induced by non-uniform shrinkage of the paste
• Possible causes of shrinkage include:
  – Autogenous (water in pores consumed by reaction)
  – Plastic (evaporation of water prior to setting)
  – Drying (evaporation of water at any stage)
  – Carbonation (dissolution/precipitation of phases due to reaction with CO₂)
THEORY OF CRACKING DUE TO DRYING

• Evaporation of water from pores causes a build up in capillary pressure

• Initially the evaporation does not empty the capillary pores inside the paste
  – Overall paste dimensions can be reduced

• Later stage involves menisci retreating into the body
  – Can reach high capillary pressure \( P_c = \frac{2\gamma_{LV}}{r_m} \)
  – Possible to induce microcracking

*Image courtesy of George Scherer*
LINK WITH PORE SIZE DISTRIBUTION

Mercury Intrusion Porosimetry
POTENTIAL SOLUTIONS TO MICROCRACKING

• Shrinkage reducing admixtures
  – Reduces the surface tension between air/water
  – Do not work for alkali-activated materials, unless at extremely high concentrations

• Crack bridging using reinforcement
  – e.g., Fibers

• Extended curing conditions

MITIGATING CRACKING WITH NANOPARTICLES?

• Nanoparticles currently used in concrete to:
  – Increase the rate of hydration
  – Increase the early age compressive strength of paste/concrete
  – Photocatalytic properties (nano-TiO$_2$)
  – Bridge cracking (using carbon nanotubes)

• Potential for nanoparticles to:
  – Alter the paste pore structure (reduce pore size so evaporation occurs only at extremely low RH)
  – Act as seeds to increase the nanostructural ordering of the paste (increase stiffness)

• In this study, we used ZnO nanoparticles (~ 35nm)
  – Stable in high pH solutions (compatible with alkaline activators)
  – Low cost (~ 1% increase in price of concrete)
  – Readily available (used in sunscreen and in solar cells)
EFFECT OF NANOPARTICLES ON MICROCRACKING

Cracked surface area (%)

- Slag 13% MgO (wt. %)
- Slag 7% MgO
- Slag 13%
- Slag 7%
- Slag 13%
- Slag 7%
- Slag 13%
- Slag 7%
- Slag 13%

1% CO₂ (63% RH)
10% CO₂ (63% RH)
Dry N₂
Air (63% RH)

Without ZnO

With ZnO

Na₂SiO₃ Activated

NaOH Activated
EFFECT OF NANOPARTICLES ON MICROCRACKING

**p**: probability that the mean values for crack surface area are equal

- **** p < 0.01%
- *** p < 0.1%
- ** p < 1%
- * p < 5%

Without ZnO

<table>
<thead>
<tr>
<th>Condition</th>
<th>Cracked surface area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% CO₂ (63% RH)</td>
<td>NaOH Activated</td>
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Slag 13% (wt.%)

Slag 13% MgO (wt.%)
IMPACT OF NANOPARTICLES ON PORE SIZE

Nitrogen Sorption

\[
\frac{dV}{d\log(r_p)} \quad (\text{mm}^3 \cdot \text{g}^{-1})
\]

\[
\text{Cum. intrusion (mm}^3 \cdot \text{g}^{-1})
\]

24h + 8h 10% CO\textsubscript{2} ZnO
24h + 8h 10% CO\textsubscript{2}
32h ZnO
32h
EFFECT ON PASTE STIFFNESS

Increasing Stiffness

Dynamic Modulus (GPa)

24h curing
24h curing + 8h 10% CO₂
32h curing

p: probability that the mean values for dynamic modulus are equal

**** p < 0.01%
*** p < 0.1%
** p < 1%
* p < 5%

Without ZnO

With ZnO

andlinger center
for energy+the environment

PRINCETON UNIVERSITY
EFFECT ON RATE OF HYDRATION

Chemical shrinkage (mL·g⁻¹)

Time (hr)

Without
With ZnO
CONCLUSIONS

• Silicate-activated slag paste is prone to extensive microcracking
  – Issue for commercialization, since silicate-activated pastes have advantageous early strength properties

• Conventional approaches to mitigating microcracking in concrete do not work for alkali-activated systems

• 0.1% wt. of nanoparticles (nano-ZnO) are seen to decrease the extent of surface microcracking
  – Does not appear to correlate with the pore size, paste stiffness or rate of hydration (strength development)
FUTURE WORK

• Use imaging (electron microscopy) to see if the pore walls are affected by the nanoparticles
  – Possible that the nanoparticles increase pore wall roughness, and prevent the evaporation of water within the pores (liquid evaporates at surface)

• Assess if nanoparticles are clogging pores at surface
  – Impact rate of evaporation

• Investigate the impact of dosage
  – Working with very small amounts (0.1% wt.) compared to conventional usage of nanoparticles in concrete (~ 5-10% wt.)
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