Mineral-Blended Polymeric Microspheres for Frost Resistance and Reduced Embodied Carbon of Concrete

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Need for Alternatives to Air Entrainment

- Air entrainment with surfactants is an effective means of achieving a freezing-and-thawing durable concrete.
- Controlling the air void system can be difficult and frustrating.
- Variability in air content of concrete due to variations in concrete materials, mixing, transportation, ambient temperature, placement method, and testing leads to problems:
  - Lower production rate of concrete
  - More rejected loads
  - Difficulty in achieving specified strength
  - Difficulty in consistently obtaining target air-void systems
  - Increased need for quality control at the project site
  - Occasionally, removal and replacement of hardened concrete that is determined to be non-compliant

Costs: Money, environmental impact, project delays…
Polymeric Microspheres

- Expanded polymeric microspheres (in powder, paste or slurry form) have been found to protect concrete from freezing-and-thawing damage since the 1970's.
  - Manufactured by suspension polymerization, then expanded to a target size by heating
- Insensitive to the factors that impact air entrainment with surfactants
- Hollow-core polymeric microspheres are dimensionally stable; and are produced as:
  - Gas-filled wet-expanded microspheres in a wet foam or slurry form, or
  - Gas-filled dry-expanded microspheres in a dry powder form
- Microspheres are engineered materials, implying a high level of consistency in their production and are commercially available

In past attempts at practical application, microspheres have tended to agglomerate, providing inconsistent performance
New Delivery Method of Microspheres – Dry Powder Form

- Blend of microspheres and mineral powder or precoated microspheres
- Results in good dispersion, consistent performance in concrete

Microsphere powder as produced tends to agglomerate

During concrete mixing, the electrostatic attraction between the microspheres and the mineral powder is broken allowing for good dispersion of the microspheres.
How Microspheres Perform in Concrete

- Microspheres have higher CTE than the concrete matrix and create annulus voids under temperature change – provide room for ice crystals to form.
- Created during freezing, but are closed when temperature rises – “on demand voids”

For most concretes ($p \leq 32\%$), $A_{\text{min}}$ is about 1.0% microsphere content by volume (which is 5 lb/yd$^3$) (dosage guidance sheet is available)

Micromechanics-based explanation

$$A_{\text{min}} = \frac{pD_e}{8\bar{s}_{\text{limit}} - D_e}$$

$A_{\text{min}}=$microsphere content by volume of concrete

$D_e =$ effective or average diameter of the microspheres

$p =$ the air-free paste content of the concrete

$\bar{s}_{\text{limit}} =$ furthest a point in the paste can be from the surface of a microsphere for the concrete to be durable

Delivery of Microspheres via Dry Powder Form

- 5 lb (2.27 kg) of the microsphere-powder blend is packaged in a commercially-available patented dissolvable paper sack or bag that disintegrates and completely disappears during concrete mixing.

- For the dosage of 5 lb/yd³, the number of 5-lb bags added to a typical concrete mixture will match the batch size in yd³.
- Round up or down to the nearest whole number of bags for the batch size.

- Bags loaded into truck, bag disintegrates within 2 min of truck mixing
- For large projects with a single concrete mixture design (concrete pavements), could be premixed with the cement.

- Using current manufacturing cost – adds $8 to $9 per cy concrete
QC – Dosage Verification in Fresh Concrete

- Truck addition: count the number of bags added
- Quality control prior to concrete placement
  - Volumetric meter test, ASTM C173, for verification of microsphere content without use of isopropyl alcohol (solvent damages microspheres).
  - Testing with air-pressure meter, ASTM C231, does not detect the presence of the microspheres. Pressures used in the test are not high enough to compress the microspheres.
  - Standards would need to be revised to accommodate this material

QC – Dosage Verification in Hardened Concrete

ASTM C457 test performed @ 200x magnification

- “Microspheres in Hardened Concrete,” ACI Concrete International, 44(3), March 2022.
## Initial Tests Using Carolinas Materials and Mixtures

<table>
<thead>
<tr>
<th>Concrete Mixtures</th>
<th>A (AEA)</th>
<th>B (microspheres)</th>
<th>C (AEA)</th>
<th>D (microspheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement (pcy)</td>
<td>574</td>
<td>101</td>
<td>500</td>
<td>167</td>
</tr>
<tr>
<td>Fly ash (pcy)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coarse Agg (pcy)</td>
<td>1871</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fine agg (pcy)</td>
<td>1102</td>
<td>1199</td>
<td>1100</td>
<td>1197</td>
</tr>
<tr>
<td>Water (pcy)</td>
<td>313</td>
<td></td>
<td>309</td>
<td></td>
</tr>
<tr>
<td>w/cm ratio</td>
<td>0.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AEA (oz/cwt)</td>
<td>0.2</td>
<td>---</td>
<td>0.21</td>
<td>---</td>
</tr>
<tr>
<td>Microspheres (pcy)</td>
<td>---</td>
<td>5.57</td>
<td>---</td>
<td>5.58</td>
</tr>
</tbody>
</table>

### Fresh Properties

<table>
<thead>
<tr>
<th></th>
<th>Unit weight (pcf)</th>
<th>% air – pressure</th>
<th>% air volumetric</th>
<th>Compressive Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>143.1</td>
<td>7.4</td>
<td>7.3</td>
<td>7-day avg (psi)</td>
</tr>
<tr>
<td></td>
<td>150.2</td>
<td>2.2</td>
<td>2.75 w/0.75 microspheres</td>
<td>4840 (23%↑)</td>
</tr>
<tr>
<td></td>
<td>144.1</td>
<td>6.8</td>
<td>7.0</td>
<td>28-day avg (psi)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.25 w/1.0 microspheres</td>
<td>4500</td>
</tr>
<tr>
<td></td>
<td>149.4</td>
<td>2.3</td>
<td></td>
<td>56-day avg (psi)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5360</td>
</tr>
</tbody>
</table>

### Compressive Strength

<table>
<thead>
<tr>
<th></th>
<th>7-day avg (psi)</th>
<th>28-day avg (psi)</th>
<th>56-day avg (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3930</td>
<td>5125</td>
<td>5635</td>
</tr>
<tr>
<td></td>
<td>4840 (23%↑)</td>
<td>6100 (19%↑)</td>
<td>7155 (27%↑)</td>
</tr>
<tr>
<td></td>
<td>3420</td>
<td>4500</td>
<td>5360</td>
</tr>
<tr>
<td></td>
<td>4220 (23%↑)</td>
<td>5630 (25%↑)</td>
<td>6955 (29%↑)</td>
</tr>
</tbody>
</table>

Increased strength offered by microsphere inclusion (due to lower air volume) offers the opportunity to reduce cement content, lowering embodied carbon.
## Freeze-Thaw Test Performance

### Concrete Mixtures

<table>
<thead>
<tr>
<th></th>
<th>A (AEA)</th>
<th>B (microspheres)</th>
<th>C (AEA)</th>
<th>D (microspheres)</th>
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</thead>
<tbody>
<tr>
<td>Cement (pcy)</td>
<td>574</td>
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<td></td>
</tr>
<tr>
<td>Water (pcy)</td>
<td>313</td>
<td>309</td>
<td></td>
<td></td>
</tr>
<tr>
<td>w/cm ratio</td>
<td>0.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AEA (oz/cwt)</td>
<td>0.2</td>
<td>---</td>
<td>0.21</td>
<td>---</td>
</tr>
<tr>
<td>Microspheres (pcy)</td>
<td>---</td>
<td>5.57</td>
<td>---</td>
<td>5.58</td>
</tr>
</tbody>
</table>

### Durability Factor (%), ASTM C666 Procedure A

<table>
<thead>
<tr>
<th>Number of Cycles</th>
<th>A (AEA)</th>
<th>B (microspheres)</th>
<th>C (AEA)</th>
<th>D (microspheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 cycles</td>
<td>98.9</td>
<td>94.1</td>
<td>94.3</td>
<td>92.2</td>
</tr>
<tr>
<td>570 cycles</td>
<td>98.4</td>
<td>92.7</td>
<td>93.8</td>
<td>92.7</td>
</tr>
<tr>
<td>630 cycles</td>
<td>96.8</td>
<td>90.3</td>
<td>95.4</td>
<td>87.5</td>
</tr>
<tr>
<td>900 cycles</td>
<td>95.9</td>
<td>81.1</td>
<td>92.3</td>
<td>69.1</td>
</tr>
</tbody>
</table>

### Mass Loss (%)

<table>
<thead>
<tr>
<th>Number of Cycles</th>
<th>A (AEA)</th>
<th>B (microspheres)</th>
<th>C (AEA)</th>
<th>D (microspheres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 cycles</td>
<td>0.45</td>
<td>0.84</td>
<td>0.25</td>
<td>1.40</td>
</tr>
<tr>
<td>570 cycles</td>
<td>0.84</td>
<td>1.62</td>
<td>0.79</td>
<td>3.02</td>
</tr>
<tr>
<td>630 cycles</td>
<td>1.09</td>
<td>2.01</td>
<td>0.97</td>
<td>3.60</td>
</tr>
<tr>
<td>900 cycles</td>
<td>1.63</td>
<td>3.24</td>
<td>1.58</td>
<td>5.36</td>
</tr>
</tbody>
</table>

At 300 cycles, DF greater than 90% for both air-entrained and microsphere concretes - excellent durability.
Mixture C after 300 F-T cycles

Mixture C after 900 F-T cycles

Mixture D after 300 F-T cycles

Mixture D after 900 F-T cycles
Additional Tests Using Carolinas Materials and Mixtures

• Two series of mixtures (25% fly ash, 30% fly ash)
• Goal: obtain data to support development of a 3-point strength vs. w/cm ratio curve (ACI 301 trial mix method) that could be used to support development and submittal of mixtures for specified strengths of 3,000 to 5,000 psi at 28 days
• All six mixtures contained microspheres – no air entraining admixture used
• Compressive strength tested, freeze-thaw testing performed ASTM C666, Procedure A through 600 cycles

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>6397</th>
<th>6398</th>
<th>6399</th>
<th>6406</th>
<th>6407</th>
<th>6408</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Fly Ash Replacement</td>
<td>25%</td>
<td>25%</td>
<td>25%</td>
<td>30%</td>
<td>30%</td>
<td>30%</td>
</tr>
<tr>
<td>w/cm ratio</td>
<td>0.55 (high)</td>
<td>0.49 (medium)</td>
<td>0.43 (low)</td>
<td>0.54 (high)</td>
<td>0.48 (medium)</td>
<td>0.42 (low)</td>
</tr>
<tr>
<td>Type I/II cement (lb/yd³)</td>
<td>415</td>
<td>465</td>
<td>530</td>
<td>384</td>
<td>432</td>
<td>493</td>
</tr>
<tr>
<td>Fly ash (lb/yd³)</td>
<td>138</td>
<td>155</td>
<td>177</td>
<td>164</td>
<td>185</td>
<td>211</td>
</tr>
<tr>
<td>Total cementitious materials content (lb/yd³)</td>
<td>553</td>
<td>620</td>
<td>707</td>
<td>548</td>
<td>617</td>
<td>704</td>
</tr>
</tbody>
</table>
Fly ash mixtures with lowest values of w/cm (< 0.45) showed a somewhat rapid decline in durability factor after 500 cycles – Not confirmed in next phase of tests.
Microsphere mixture performance in ASTM C666 Procedure A

- 6397 (25% ash, 0.55 w/cm)
- 6406 (30% ash, 0.54 w/cm)
- 6398 (25% ash, 0.49 w/cm)
- 6407 (30% ash, 0.48 w/cm)
- 6399 (25% ash, 0.43 w/cm)
- 6408 (30% ash, 0.42 w/cm)
Mixture 6406
30% ash, 0.54 w/cm after 300 F-T cycles

Mixture 6406
30% ash, 0.54 w/cm after 600 F-T cycles

Mixture 6408
30% ash, 0.42 w/cm after 300 F-T cycles

Mixture 6408
30% ash, 0.42 w/cm after 600 F-T cycles
Findings

- All microsphere mixtures in this series had DF near 100 at 300 cycles, exhibiting excellent performance
- Most microsphere mixtures in this series showed DF near 100% up to about 500 cycles
- After 500 cycles, mixtures with lowest w/cm ratios began to decline more rapidly

- After 600 cycles (2x typical test duration), the DF of each microsphere mixture was greater than 70%
- Four mixtures (25% fly ash at 0.55 and 0.49 w/cm ratio, and 30% fly ash at 0.54 and 0.48 w/cm ratio) retained DF of nearly 100% after 600 cycles.

- Lowest w/cm mixtures exhibited the lowest mass loss at both 25% and 30% fly ash levels.
- Mixtures with w/cm above 0.50 exhibited higher mass loss at both levels of fly ash

- Results indicated that use of fly ash as high as 30% may need to be limited to microsphere concrete with w/cm between 0.45 and 0.50 to achieve a good resistance to mass loss and a high durability factor.
More Tests Using Carolinas Materials and Mixtures

- Three sets of mixtures designed to meet local/state specifications
- Goal 1: Develop microsphere mixtures that should compare similarly in strength to typical mixtures used for local/NCDOT purposes
- Goal 2: Explore potential global warming potential (GWP) reduction
  - Note: does not include GWP of microspheres – yet to be established (likely to be very small compared to the GWP of cement removed)

<table>
<thead>
<tr>
<th>Description</th>
<th>NCDOT Class AA 4,500 psi</th>
<th>City of Charlotte 3,600 psi</th>
<th>NCDOT Class B 2,500 psi</th>
<th>NCDOT Class A 3,000 psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture ID</td>
<td>6915</td>
<td>6916</td>
<td>6917</td>
<td>6918</td>
</tr>
<tr>
<td>freeze-thaw approach</td>
<td>AEA</td>
<td>Microsp.</td>
<td>AEA</td>
<td>Microsp.</td>
</tr>
<tr>
<td>% fly ash</td>
<td>23.1</td>
<td>30</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>cement (pcy)</td>
<td>572</td>
<td>493</td>
<td>523</td>
<td>409</td>
</tr>
<tr>
<td>fly ash (pcy)</td>
<td>172</td>
<td>211</td>
<td>131</td>
<td>175</td>
</tr>
<tr>
<td>Design/actual w/cm ratio</td>
<td>0.39 / 0.39</td>
<td>0.426 / 0.426</td>
<td>0.46 / 0.427</td>
<td>0.50 / 0.50</td>
</tr>
<tr>
<td>GWP (kg CO₂eq pcy)</td>
<td>253</td>
<td>225</td>
<td>234</td>
<td>192</td>
</tr>
<tr>
<td>Reduction in GWP (%)</td>
<td>---</td>
<td>11.07</td>
<td>---</td>
<td>17.95</td>
</tr>
</tbody>
</table>
Performance in ASTM C666 Procedure A

Durability factors of fly ash mixtures with w/cm < 0.45 remained stable beyond 500 cycles, contrary to results in the earlier tests.
Performance in ASTM C666 Procedure A

Number of Cycles

% change in weight

6915 (AEA, 23.1% fly ash, w/cm 0.39)
6916 (microsp, 30% fly ash, 0.426 w/cm)
6917 (AEA, 20% fly ash, 0.427 w/cm)
6918 (microsp, 30% fly ash, 0.50 w/cm)
6954 (AEA, 23.2% fly ash, 0.47 w/cm)
6955 (microsp, 30% fly ash, 0.532 w/cm)
Mixture 6915
23.1% ash, 0.39 w/cm after 300 F-T cycles

Mixture 6915
23.1% ash, 0.39 w/cm after 600 F-T cycles

Mixture 6916
30% ash, 0.426 w/cm after 300 F-T cycles

Mixture 6916
30% ash, 0.426 w/cm after 600 F-T cycles
Mixture 6954
23.2% ash, 0.47 w/cm after 300 F-T cycles

Mixture 6954
23.2% ash, 0.47 w/cm after 600 F-T cycles

Mixture 6955
30% ash, 0.532 w/cm after 300 F-T cycles

Mixture 6955
30% ash, 0.532 w/cm after 600 F-T cycles
Findings

- 28-day compressive strengths for both AEA and microsphere mixtures met respective targets.

- After 300 cycles, microsphere mixtures exhibited DF not less than around 90% (89.4%).

- Microsphere mixtures continued to show suitable durability performance up to 600 cycles.

- Microsphere mixtures with $w/cm$ greater than or equal to 0.50 at a 30% fly ash replacement rate exhibited high mass loss in the study relative to mixtures with $w/cm$ below 0.50.
  - Severe winter conditions
    - $w/cm$ may need to be limited to below 0.50 with fly ash at 30%.
  - Mild winter exposure conditions
    - $w/cm$ in the range of 0.50 to 0.55 may provide adequate performance.
Findings

- Additional study may be warranted to understand the role, if any, of stiffness of low w/cm concretes in the freeze-thaw performance of microsphere concrete.

- Significant benefit of a lower w/cm was observed in both parts of the study by the lower mass losses for the microsphere concrete mixtures with 30% fly ash and w/cm in the range of 0.42 to 0.48 compared with the mass losses for mixtures with w/cm higher than 0.50.
Conclusions – Sustainability Benefits

- Microspheres are insensitive to factors that cause problems with surfactant air entrainment
- Can provide a reliable alternative technology for achieving a frost-resistant concrete.
  - Could reduce the need to reject truck loads of concrete due to improper levels of air entrainment, thereby reducing waste.
- Can avoid the strength loss caused by air entrainment
  - Cement contents can be reduced in the range of 10 to 20% to achieve compressive strength comparable to that of air-entrained concrete
  - Can allow for replacement of cement with fly ash or other SCMs at higher levels
  - Can allow use of fly ash with high unburned carbon content.
  - Embodied carbon contents as measured by the calculated GWP values for the microsphere concrete mixtures with a 30% fly ash content are 11% to 18% lower than the GWP values for the corresponding conventional air-entrained concrete mixtures
Conclusions – Potential Constructability Benefits

• Could eliminate or reduce the production and placement issues related to pumped air-entrained concrete.

• Allows for dense, polished, machine-troweled surfaces to be specified for concrete slabs in freezing-and-thawing environments.

• Can increase productivity and potentially lower concrete production costs by not having personnel to constantly check and manage air-entrained concrete.

• Could support development of concrete mixtures with a stiff consistency that are difficult to air entrain, such as pervious concrete and roller-compact ed concrete, to show improved freeze-thaw resistance.
Acknowledgments

- Clarke Summers, Brandon Ellis, Siva Sikhakolli – UNC Charlotte
- Dustin Heiland – Concrete Supply Co.

Supporting Publications