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

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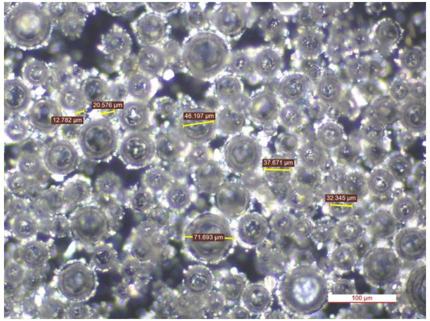

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Need for Alternatives to Air Entrainment

- 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.

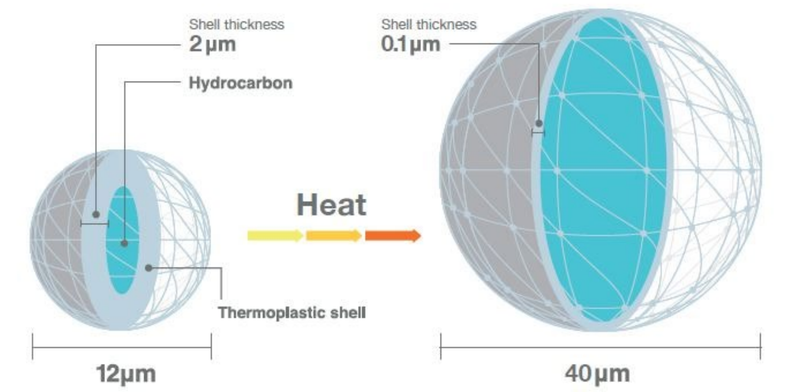
- Variability in air content of concrete due to variations in concrete materials, mixing, transportation, ambient temperature, placement method, and testing leads to problems:
    - Lower production rate of concrete
    - More rejected loads
    - Difficulty in achieving specified strength
    - Difficulty 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

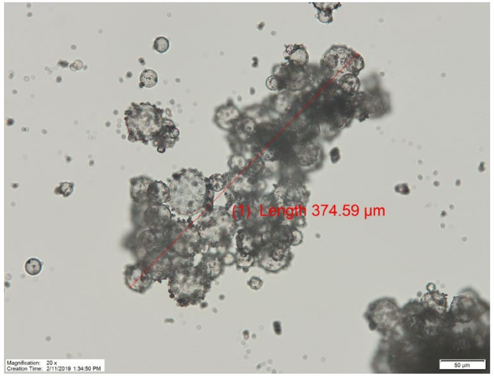
- Expanded polymeric microspheres (in powder, paste or slurry form) have been found to protect concrete from freezing-and-thawing damage since the 1970’s.
    - Manufactured by suspension polymerization, then expanded to a target size by heating
- Insensitive to the factors that impact air entrainment 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



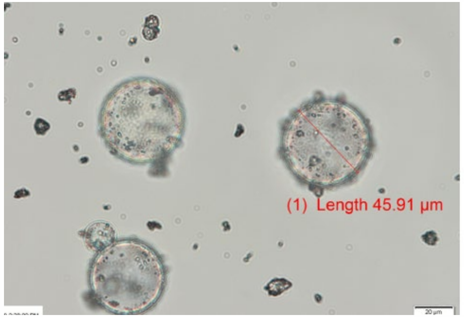
New Delivery Method of Microspheres – Dry Powder Form

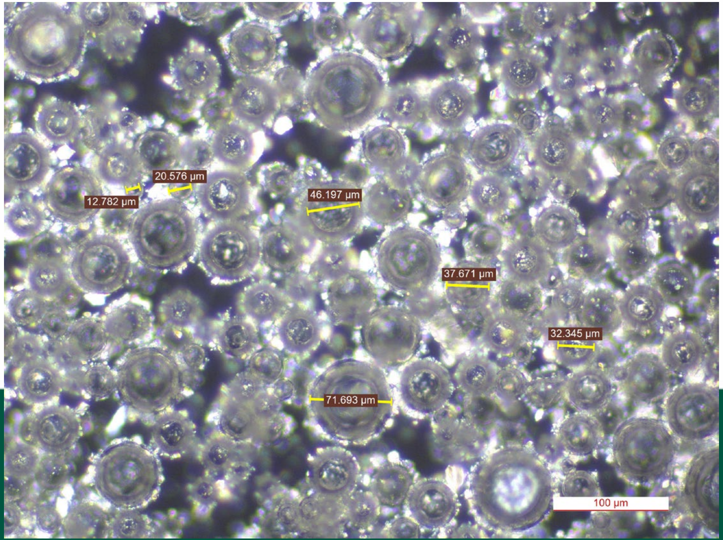
- Blend of microspheres and mineral powder or precoated microspheres
- Results in good dispersion, consistent performance in concrete



Microsphere powder as produced tends to agglomerate

Powder blend with mineral powder coating: well-dispersed microspheres

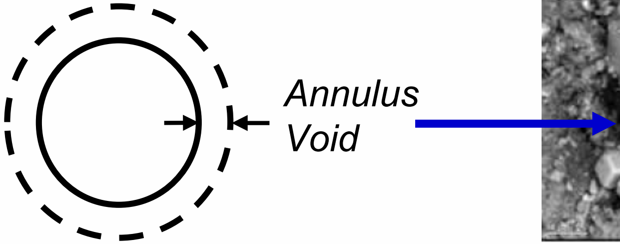




During concrete mixing, the electrostatic attraction between the microspheres and the mineral powder is broken allowing for good dispersion of the microspheres.

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”



Microsphere at a freezing temperature
(Moffatt & Thomas, *CI* 2019)

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

Micromechanics-based explanation

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

A_{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

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

“Compliance Concept in Protection of Concrete from Freezing-and-Thawing Damage,” *ACI Materials Journal*, V. 117, No. 6, Nov.-Dec. 2020.

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/yd^3, the number of 5-lb bags added to a typical concrete mixture will match the batch size in yd^3.
- Round up or down to the nearest whole number of bags for the batch size.

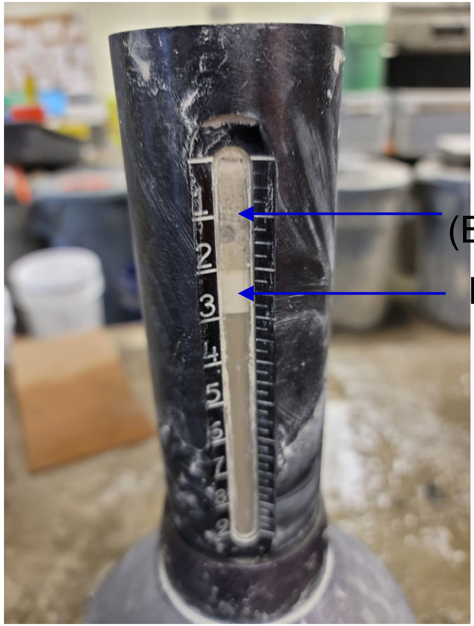
- Bags loaded into truck, bag disintegrates within 2 min of truck mixing
- For large projects with a single concrete mixture design (concrete pavements), could be premixed with the cement.

- Using current manufacturing cost – adds $8 to $9 per cy concrete

QC – Dosage Verification in Fresh Concrete

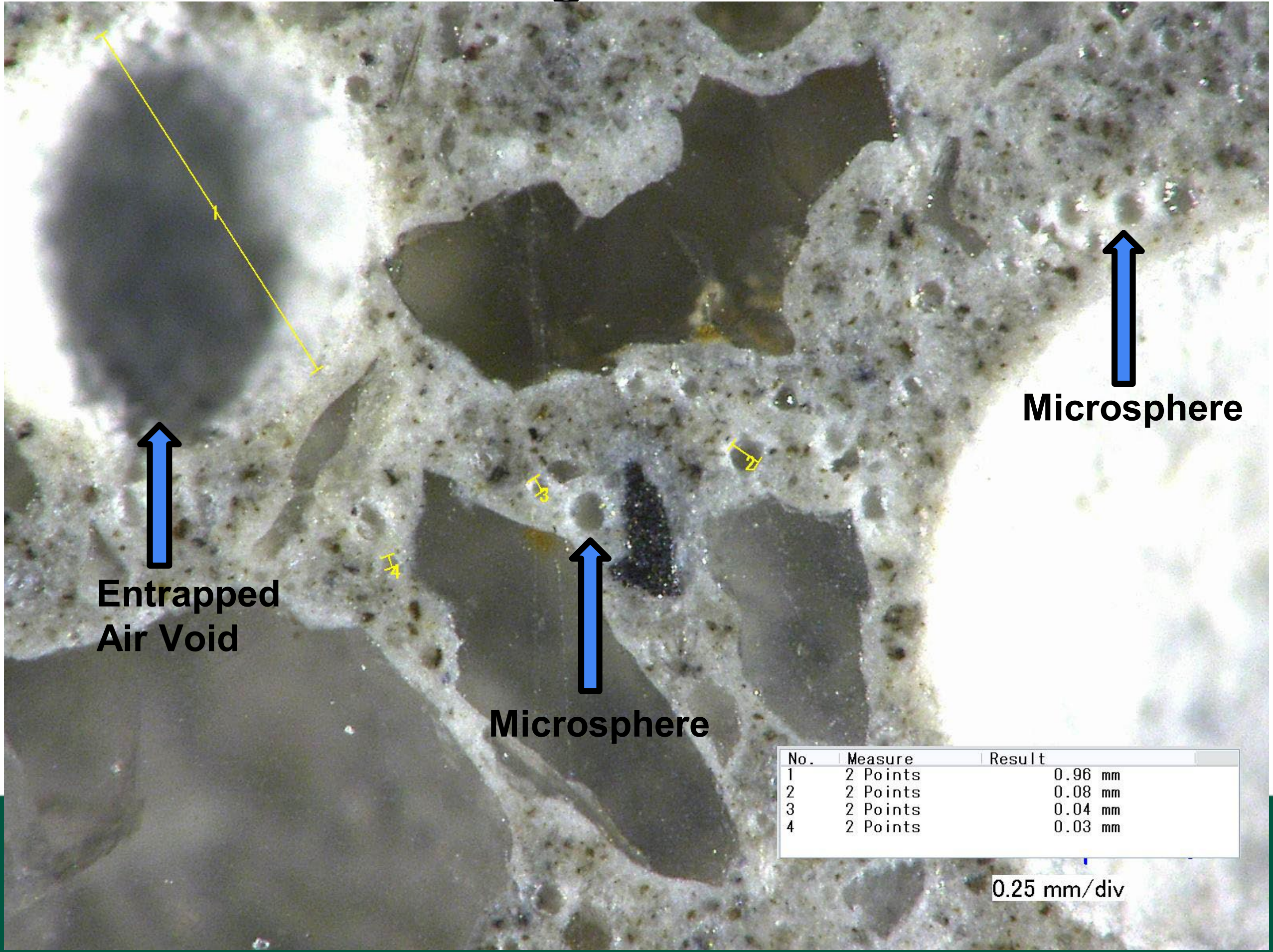
- Truck addition: count the number of bags added

- 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



“A New Way to Deliver Protection from Freezing-and-Thawing Damage,” *ACI Concrete International*, V. 43, No. 1, Jan. 2021.

QC – Dosage Verification in Hardened Concrete



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No.   Measure    Result
1     2 Points          0.96 mm
2     2 Points          0.08 mm
3     2 Points          0.04 mm
4     2 Points          0.03 mm
```

ASTM C457 test performed @ 200x magnification

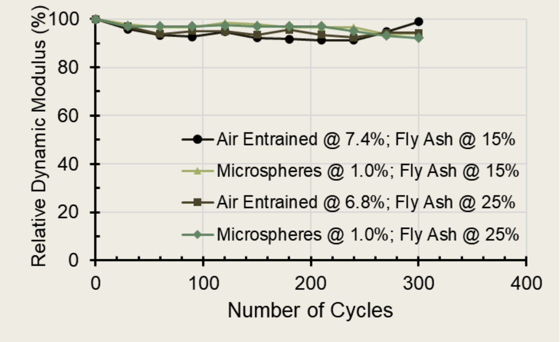
- “Microspheres in Hardened Concrete,” *ACI Concrete International*, 44(3), March 2022.
- “Predicting the Magnitude of Microsphere Parameters obtained from Microscopical Examination of Hardened Concrete,” *ASTM Journal of Testing and Evaluation*, V. 51, No. 5, Sept./Oct. 2023, https://doi.org/10.1520/JTE20220469

Initial Tests Using Carolinas Materials and Mixtures

	Concrete Mixtures			
	A (AEA)	B (microspheres)	C (AEA)	D (microspheres)
Cement (pcy)	574		500	
Fly ash (pcy)	101		167	
Coarse Agg (pcy)	1871			
Fine agg (pcy)	1102	1199	1100	1197
Water (pcy)	313		309	
w/cm ratio	0.46			
AEA (oz/cwt)	0.2	---	0.21	---
Microspheres (pcy)	---	5.57	---	5.58
Fresh Properties				
Unit weight (pcf)	143.1	150.2	144.1	149.4
% air – pressure	7.4	2.2	6.8	2.3
% air volumetric	7.3	2.75 w/0.75 microspheres	7.0	3.25 w/1.0 microspheres
Compressive Strength				
7-day avg (psi)	3930	4840 (23%↑)	3420	4220 (23%↑)
28-day avg (psi)	5125	6100 (19%↑)	4500	5630 (25%↑)
56-day avg (psi)	5635	7155 (27%↑)	5360	6955 (29%↑)

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



At 300 cycles, DF greater than 90% for both air-entrained and microsphere concretes - excellent durability

	Concrete Mixtures			
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w/cm ratio	0.46			
AEA (oz/cwt)	0.2	---	0.21	---
Microspheres (pcy)	---	5.57	---	5.58
Durability Factor (%), ASTM C666 Procedure A				
300 cycles	98.9	94.1	94.3	92.2
570 cycles	98.4	92.7	93.8	92.7
630 cycles	96.8	90.3	95.4	87.5
900 cycles	95.9	81.1	92.3	69.1
Mass Loss (%)				
300 cycles	0.45	0.84	0.25	1.40
570 cycles	0.84	1.62	0.79	3.02
630 cycles	1.09	2.01	0.97	3.60
900 cycles	1.63	3.24	1.58	5.36

Mixture A after
300 F-T cycles

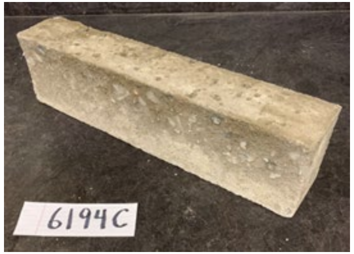
Mixture A after
900 F-T cycles

Mixture B after
300 F-T cycles

Mixture B after
900 F-T cycles

Mixture C after
300 F-T cycles

Mixture C after
900 F-T cycles



Mixture D after
300 F-T cycles

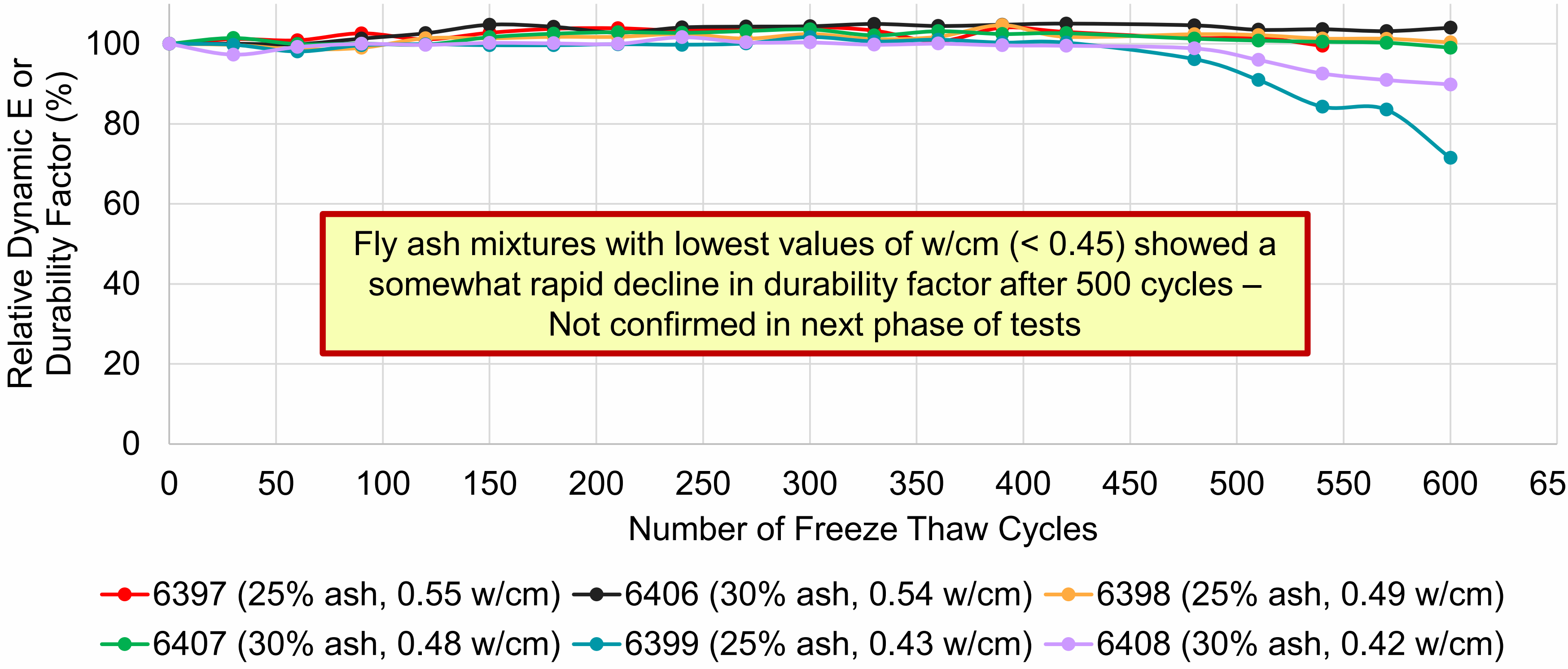
Mixture D after
900 F-T cycles

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

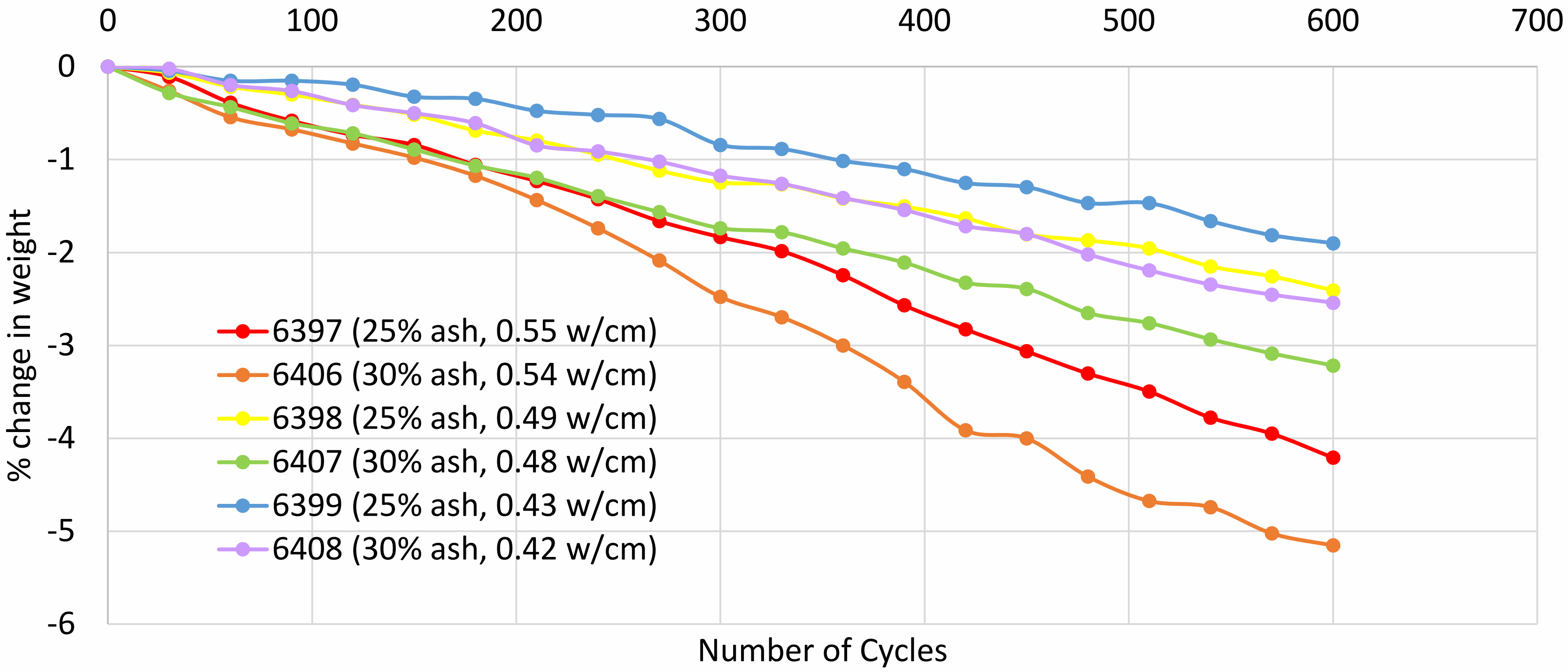
Mixture ID	**6397**	**6398**	**6399**	**6406**	**6407**	**6408**
% Fly Ash Replacement	25%			30%		
w/cm ratio	0.55 (high)	0.49 (medium)	0.43 (low)	0.54 (high)	0.48 (medium)	0.42 (low)
Type I/II cement (lb/yd^3)	415	465	530	384	432	493
Fly ash (lb/yd^3)	138	155	177	164	185	211
Total cementitious materials content (lb/yd^3)	553	620	707	548	617	704

Microsphere mixture performance in ASTM C666 Procedure A



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



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

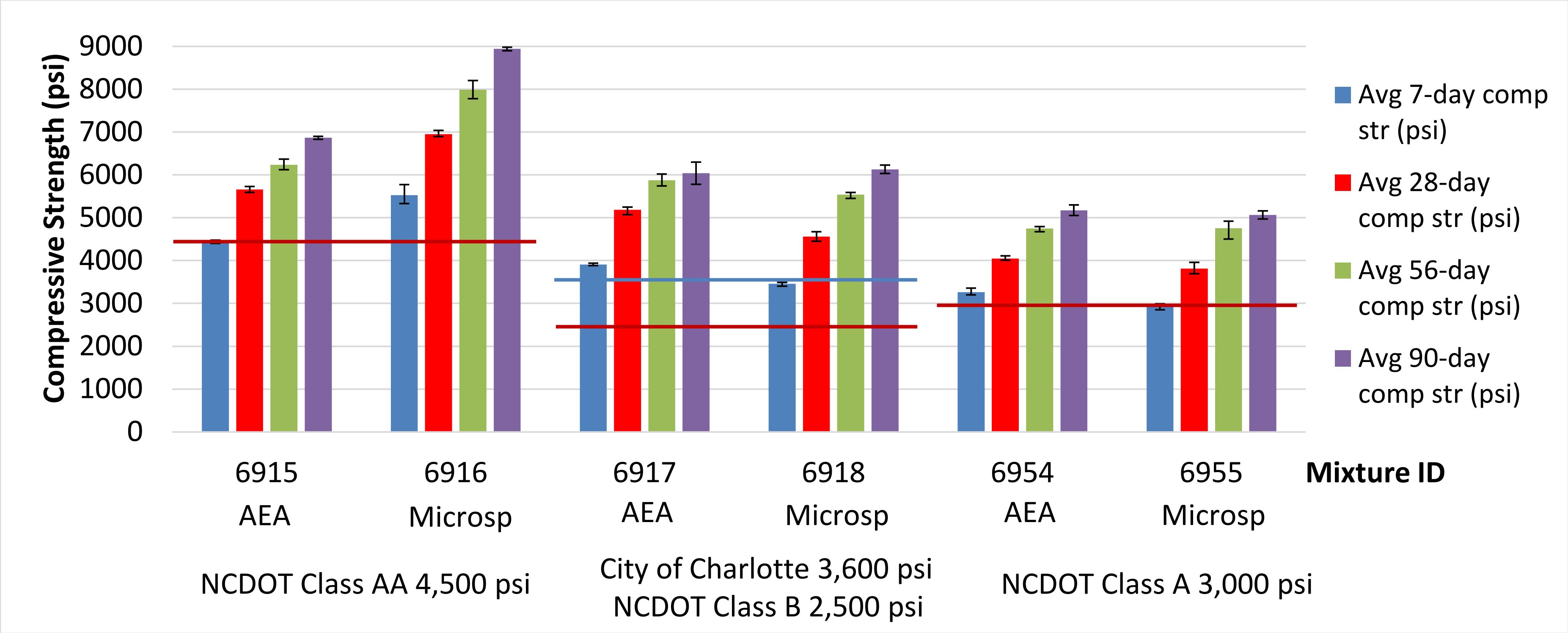
- Results indicated that use of fly ash as high as 30% may need to be limited to microsphere concrete with w/cm between 0.45 and 0.50 to achieve a good resistance to mass loss and a high durability factor.

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)

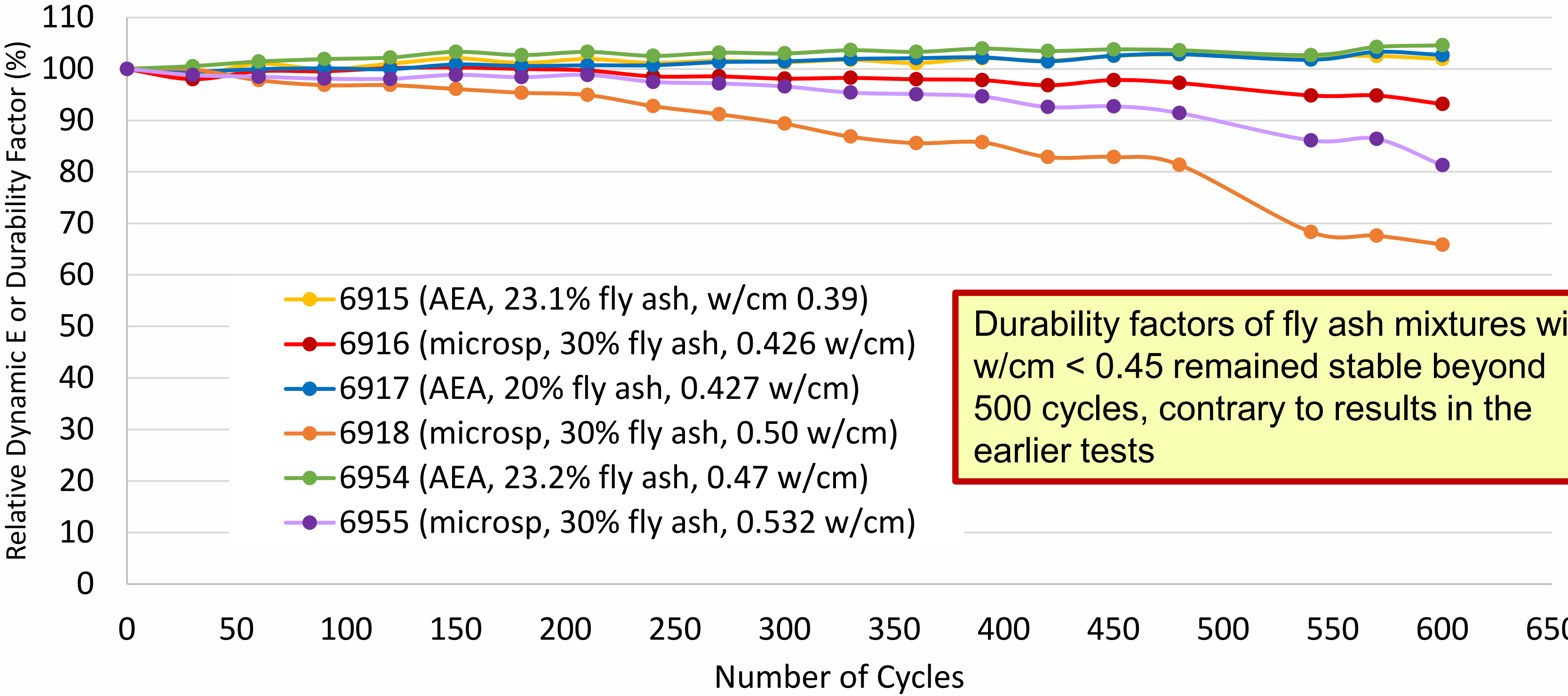
Description	**NCDOT Class AA 4,500 psi**		**City of Charlotte 3,600 psi NCDOT Class B 2,500 psi**		**NCDOT Class A 3,000 psi**	
Mixture ID	**6915**	**6916**	**6917**	**6918**	**6954**	**6955**
freeze-thaw approach	AEA	Microsp.	AEA	Microsp.	AEA	Microsp.
% fly ash	23.1	30	20	30	23.2	30%
cement (pcy)	572	493	523	409	451	384
fly ash (pcy)	172	211	131	175	136	165
Design/actual w/cm ratio	0.39 / 0.39	0.426 / 0.426	0.46 / 0.427	0.50 / 0.50	0.47 / 0.47	0.532 / 0.532
GWP (kg CO_2eq pcy)	253	225	234	192	207	182
Reduction in GWP (%)	---	11.07	---	17.95	---	12.08

Compressive strength test results



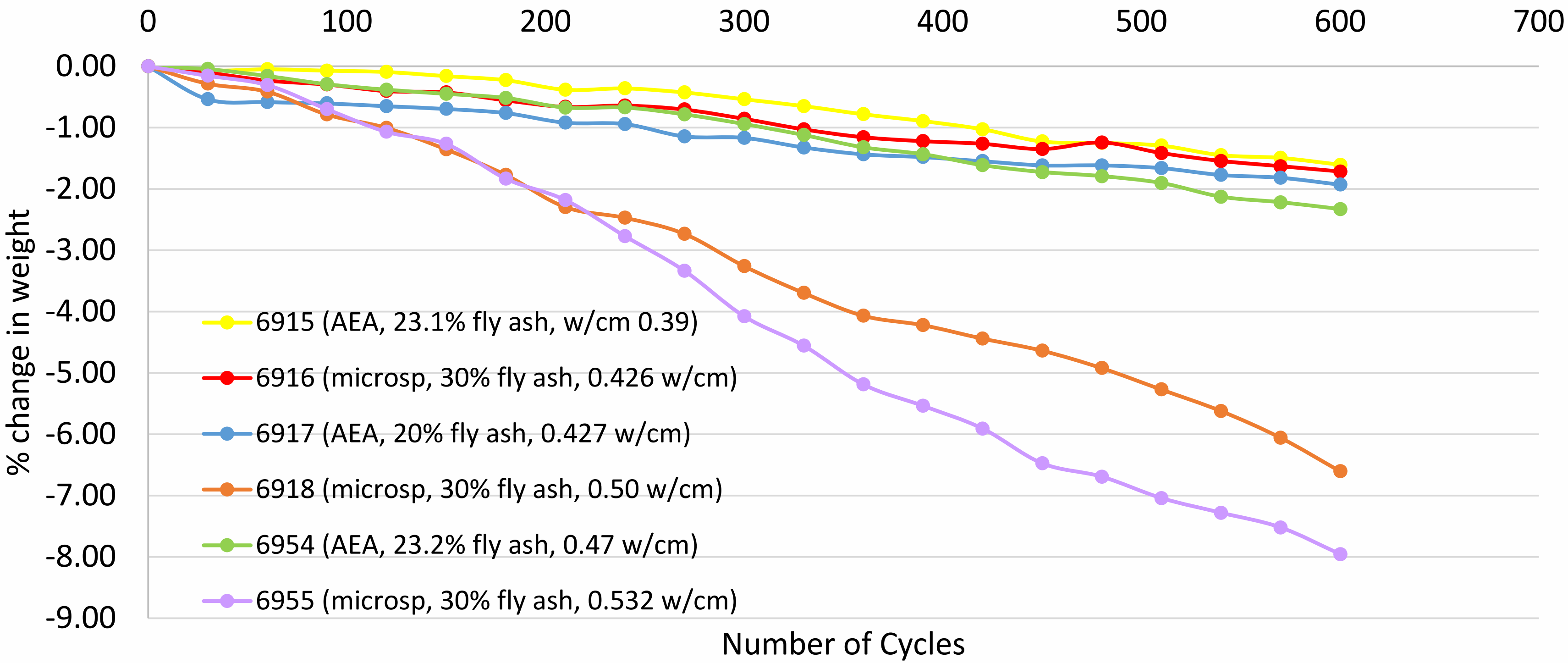
🟥 = specified compressive strength NCDOT
🟦 = specified compressive strength City of Charlotte

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



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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

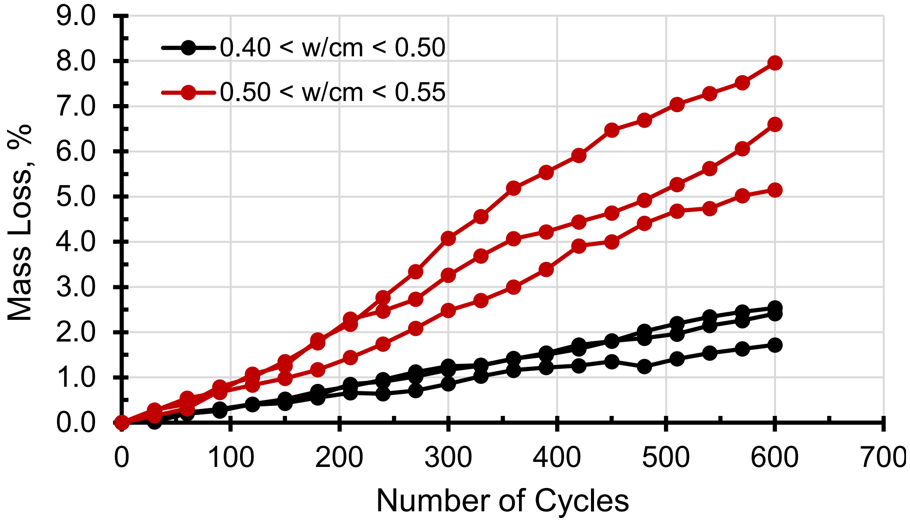
Findings

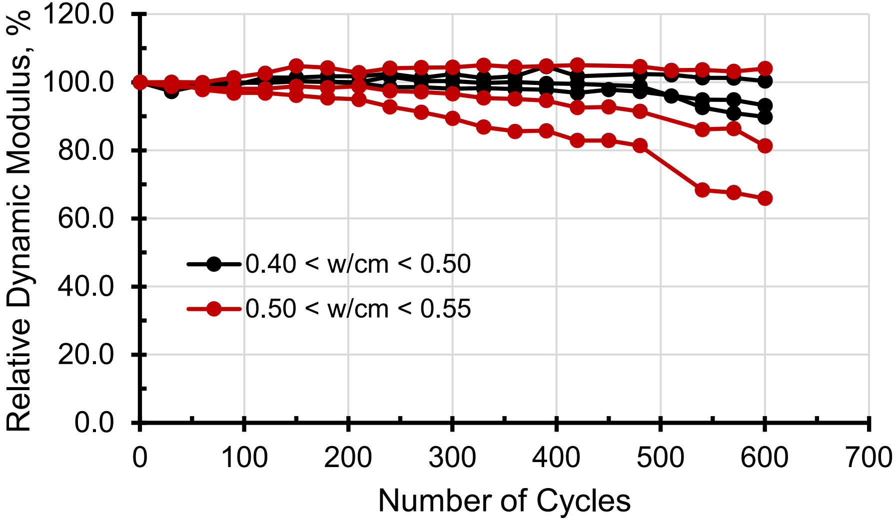
- 28-day compressive strengths for both AEA and microsphere mixtures met respective targets
- After 300 cycles, microsphere mixtures exhibited DF not less than around 90% (89.4%)
- Microsphere mixtures continued to show suitable durability performance up to 600 cycles
- Microsphere mixtures with w/cm 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-compacted concrete, to show improved freeze-thaw resistance.

Acknowledgments

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

Supporting Publications

- Attiogbe, E.K., Cavalline, T.L., and Neuwald, A.D., “Lowering Carbon Footprint While Achieving Frost-Resistant Concrete,” *ACI Concrete International*, V. 45, No. 5, May 2023, pp. 36-41.
- Attiogbe, E.K., “A New Way to Deliver Protection from Freezing-and-Thawing Damage,” *ACI Concrete International*, V. 43, No. 1, Jan. 2021, pp. 27-33.
- Attiogbe, E.K., “Compliance Concept in Protection of Concrete from Freezing-and-Thawing Damage,” *ACI Materials Journal*, V. 117, No. 6, Nov.-Dec. 2020, pp.187-200.
- Attiogbe, E.K., “Microspheres in Hardened Concrete,” *ACI Concrete International*, V. 44, No. 3, Mar. 2022, pp. 43-50.
- Attiogbe, E.K., “Predicting the Magnitude of Microsphere Parameters obtained from Microscopical Examination of Hardened Concrete,” *ASTM Journal of Testing and Evaluation*, V. 51, No. 5, Sept./Oct. 2023, pp. 3418-3434, https://doi.org/10.1520/JTE20220469
- Attiogbe, E.K., *Method of Delivery of Dry Polymeric Microsphere Powders for Protecting Concrete from Freeze-Thaw Damage*, U.S. Patent 10,730,794 B1, filed Sept. 30, 2019, and issued Aug. 4, 2020.