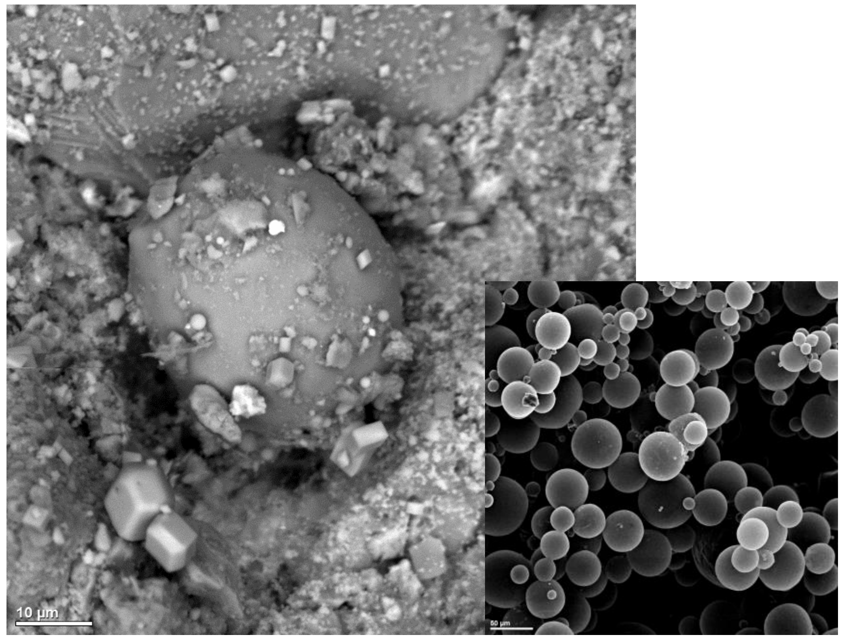
Use of Polymeric Microspheres for Providing Resistance to Freeze-Thaw and Salt Scaling



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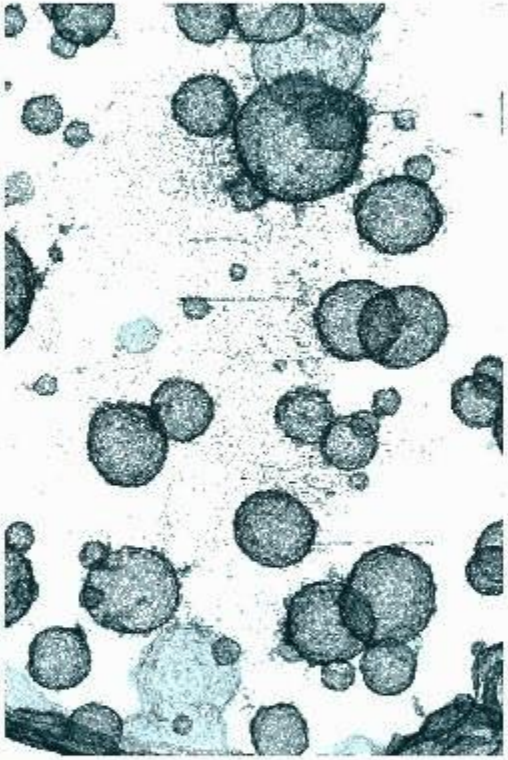
Technical Session on *New Innovations in Chemical Admixtures* – ACI Spring Convention – Salt Lake City, March 25 – 29, 2018

Issues with Entrained Air

- Control of air content
  - Affected by concrete materials, mixture proportions, mixing, transportation, construction practices, and ambient conditions.
- Strength loss
  - Approx. 5% strength reduction for every 1% air
  - Increase in cement content often required to compensate
- Difficulty measuring L-bar (in fresh concrete)



History

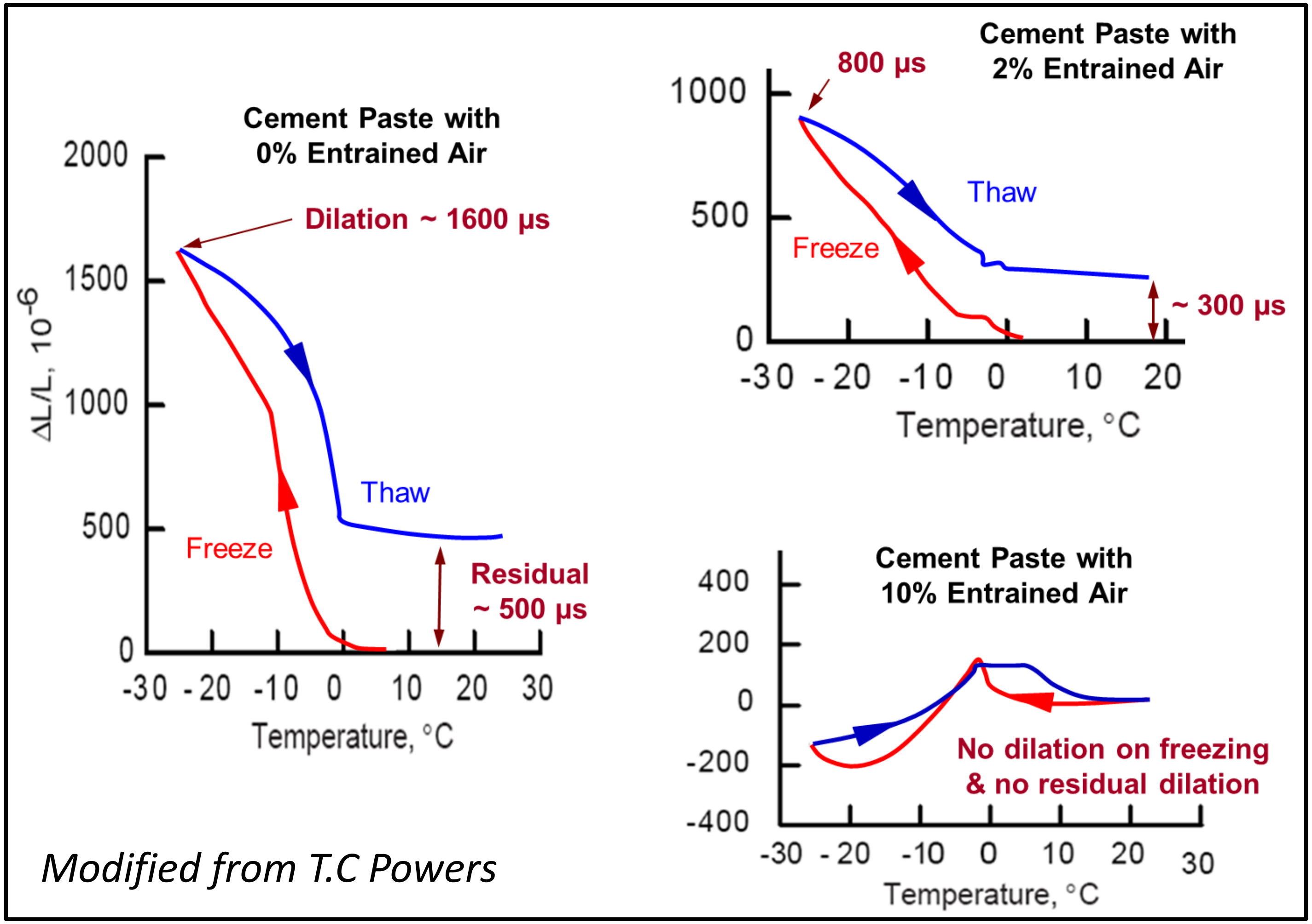
- De Rook, 1976. ”Process for preparing frost-resistant concrete.” U.S. Patent (originally filed in the Netherlands in 1975)
  - A process for making frost-resistant concrete having improved 28-day compressive strength
  - Dispersing gas-filled synthetic polymeric spheres (10 to 100 μm) in the cement product at about 0.01 to 0.1% by weight of cement
  - According to the invention, for instance, a considerable increase in frost resistance is obtained even when use is made of only a very small amount of as little as
  - 0.015% by weight (calculated on the dry cement weight) of spheres with an average particle size of 40 μm. **Such an addition is found to correspond to a volume percentage of air of as little as 0.26%.**

History

- Sommer, 1978. ”A new method for making concrete resistant to frost and de-icing salts.” Betonwerk Fertigteit-Technick, **9**, pp. 476-484
  - Hollow plastic microspheres between 10 and 60 µm added to concrete
  - Addition of 1% by weight of cement corresponds to 0.7% by volume of concrete
  - Spacing factor equivalent is 0.07 mm (70 µm)
  - 1% microsphere as effective as 5% air
  - Similar workability improvement
  - Slight increase in strength (40 MPa at 1% microspheres and 38 MPa at 5% air)
- Vanhanen, 1980. ”Air-entraining agents for frost resitance of concrete.” Lab Report No. 73, Tech. Res. Centre, Finland
  - Minimum amount of 0.6% microsphere was needed for good frost resistance
  - Compressive strength of air-entrained concrete less than that containing microspheres

History

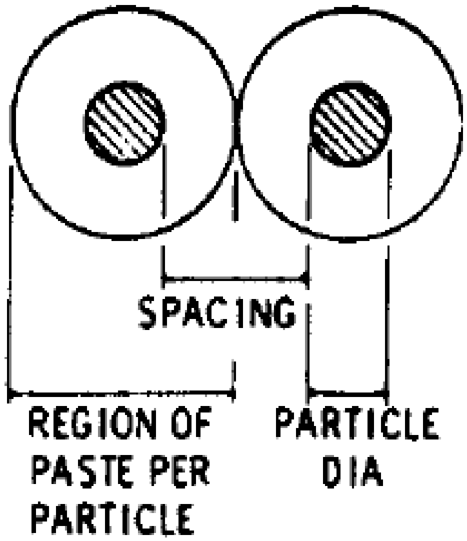
- Litvan & Sereda, 1979. "Particulate admixture for enhanced freeze-thaw resistance of concrete." Cement & Concrete Research, Vol. 8, pp. 53-60



Modified from T.C Powers

History

- Litvan & Sereda, 1979. ”Particulate admixture for enhanced freeze-thaw resistance of concrete.” Cement & Concrete Research, Vol. 8, pp. 53-60
  - Incorporation of porous particles with at least 30 per cent total porosity and pore diameters, mainly between 0.3 and 2 microns, added to the plastic mix were found to improve significantly the freeze-thaw resistance of hydrated neat cement paste and concrete.
  - The concentration required for the achievement of a given level of frost resistance depends on the physical characteristics of the material.
  - 16% brick particles (0.5 ± 0.08 mm in size, 36% total porosity) were effective
  - Incorporation of porous particles as admixtures eliminates the problems due to the instability and strength reducing effect of conventionally entrained air bubbles.

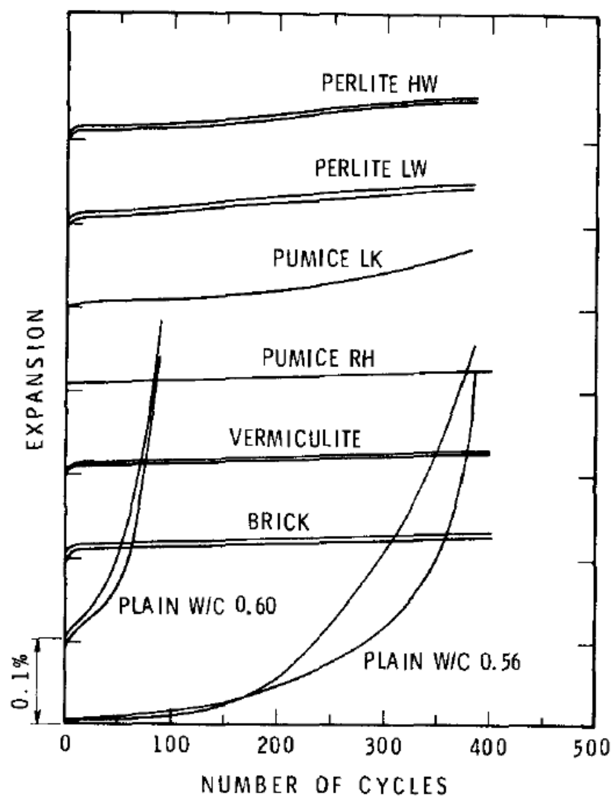


History

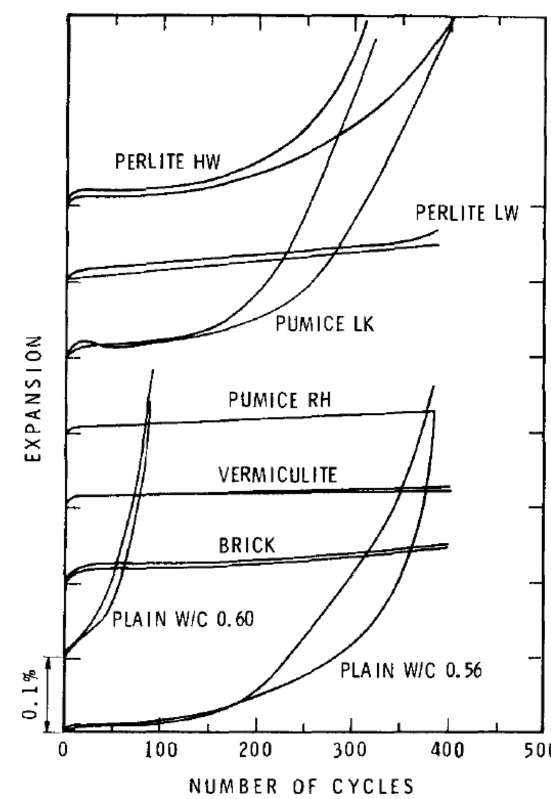
- Litvan, 1985. " Further Study of Particulate Admixtures for Enhanced Freeze-Thaw Resistance of Concrete." ACI Journal, Sept-Oct, pp. 724-730
  - Brick A (from previous study), vermiculite, pumice (x2), perlite (x2)

- Freeze-thaw cycles to produce residual expansion of 0.1%
- Test to 400 cycles
- Concrete without particulate admixture; w/cm = 0.56 & 0.60
- Concrete with particulate admixture; w/cm = 0.63

High Concentration



Low Concentration



- Technology developed in Europe
- Transportation of expanded spheres is costly
- BASF technology (patents pending) “point-of-use” system
  - Liquid polymer delivered to concrete producer
  - Processed at the concrete plant to produce expanded particles

Test Program

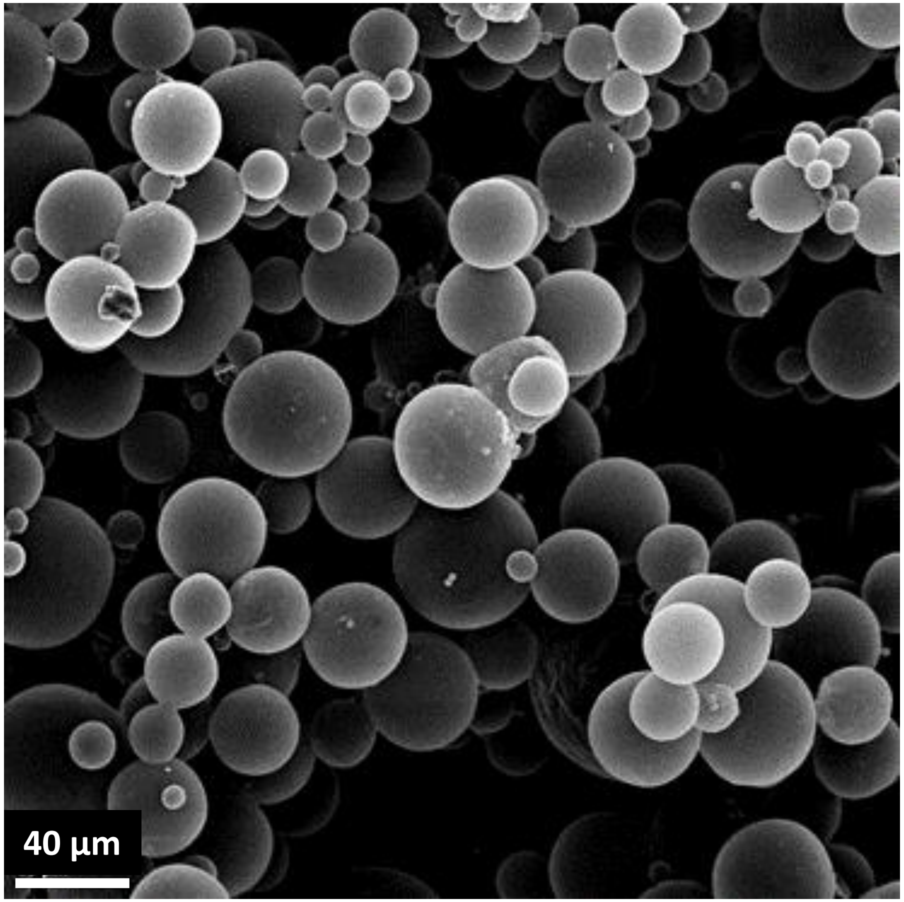
- Concrete mixtures produced with w/cm = 0.42 & target slump = 150 mm (6 in.)
    1. Ref: target air = 6%
    2. MS-075: 0.75% MS (by volume)
    3. MS-100: 1.00% MS (by volume)
- Compressive strength
- Freeze-thaw: ASTM C 666 Procedure A
- Salt scaling: ASTM C 672
- Slabs (600 x 600 mm, 24 x 24 in.) on UNB exposure site
- Prisms (150 x 150 x 525 mm, 6 x 6 x 21 in.) in tidal zone at Treat Island

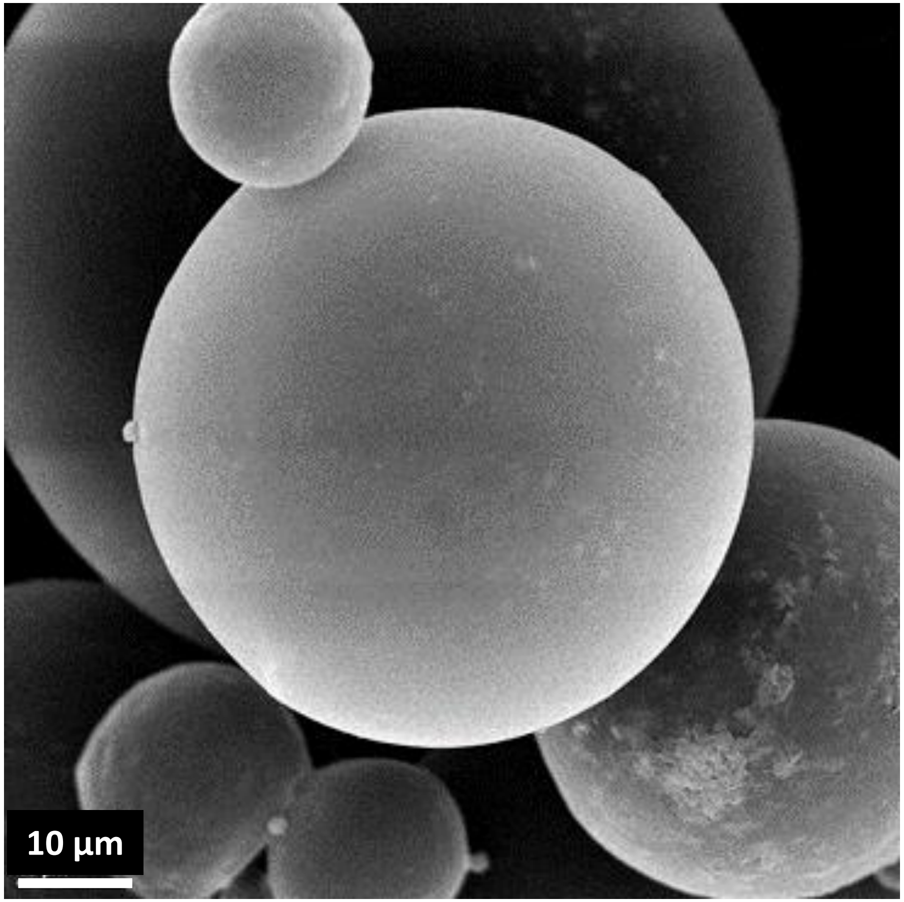
Concrete Mixture Proportions (SI)

Mixture	Proportions (kg/m³)				AEA dosage (mL/100kg)	Microsphere admixture, % by volume
	Portland cement	Fine aggregate	Coarse aggregate	Water		
Reference	400	729	980	168	98	-
MS-075		842	980		-	0.75
MS-100		835	980		-	1.00

Concrete Mixture Proportions (inch-pound)

Mixture	Proportions (pcy)				AEA dosage (fl oz/cwt)	Microsphere admixture, % by volume
	Portland cement	Fine aggregate	Coarse aggregate	Water		
Reference	667	1215	1633	280	1.50	-
MS-075		1403	1633		-	0.75
MS-100		1391	1633		-	1.00

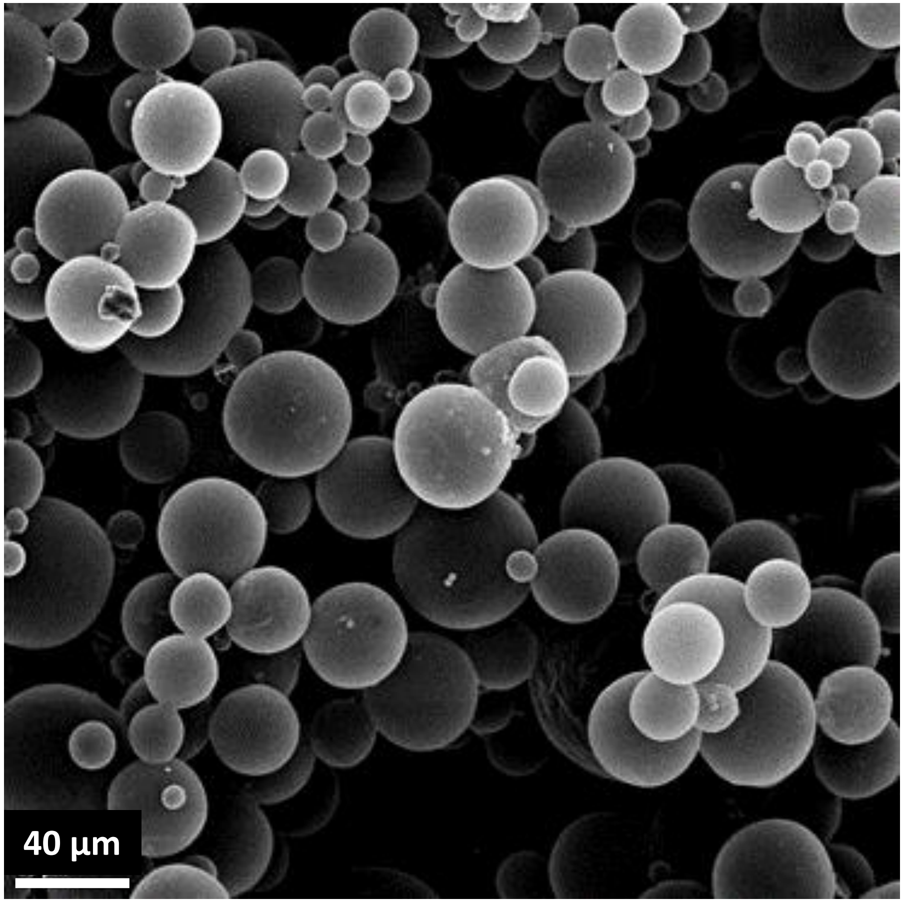


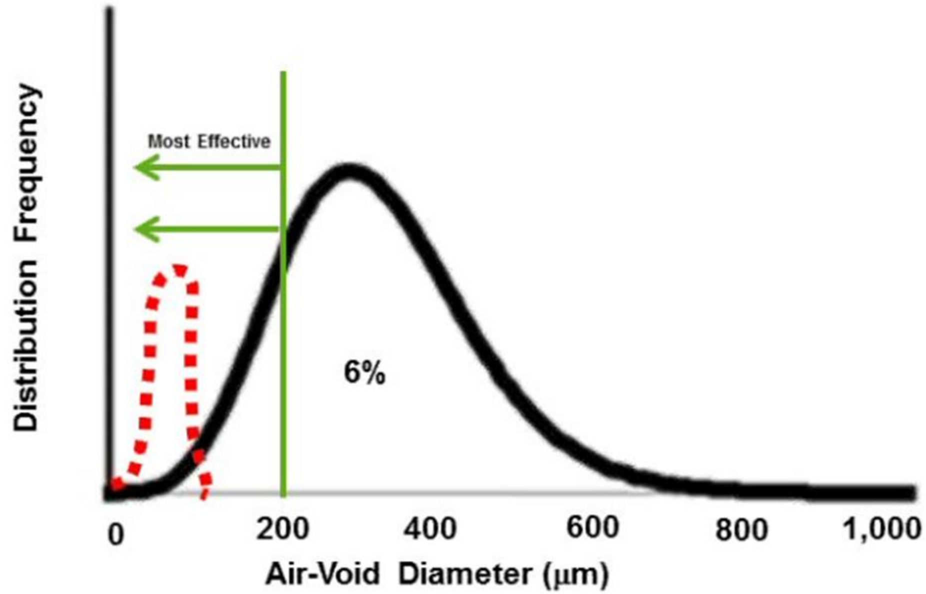


Polymeric microspheres with nominal diameter of 40 µm

Note: 1 µm = 40 x 10^{-6} in.

Microspheres provided to UNB as a slurry (from BASF)





A 1%-dose (by volume) of 40-µm spheres produces 22,000,000 spheres per cubic foot of concrete

Statistics courtesy of BASF

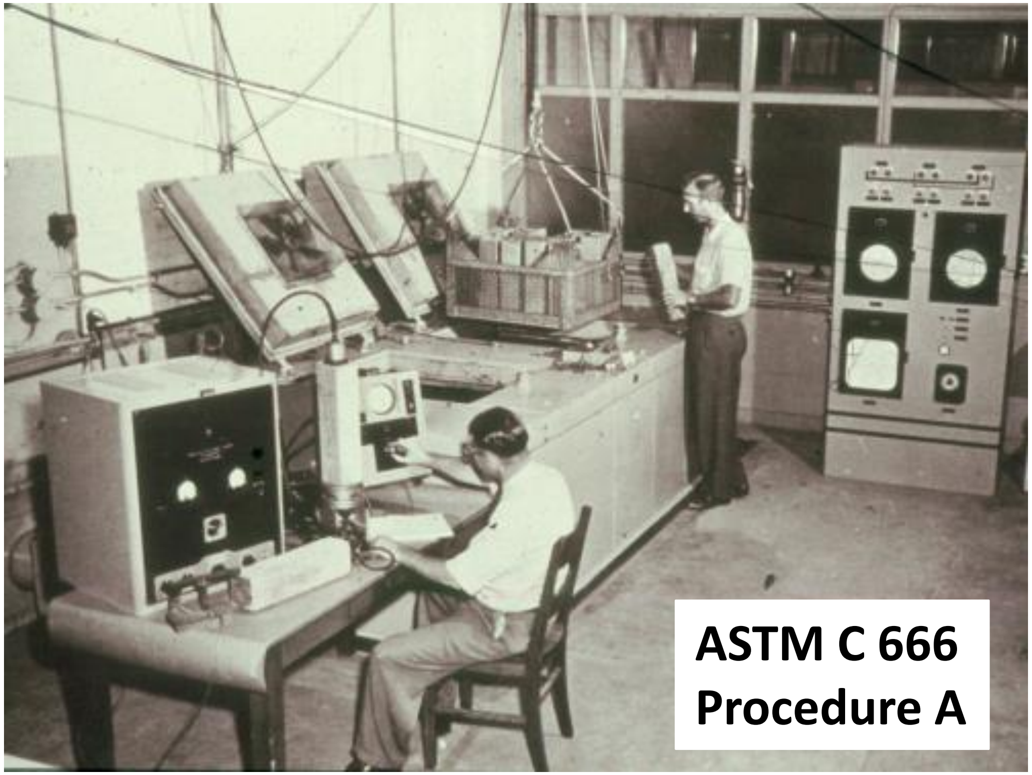
Concrete Properties (SI)

Mixture	Fresh Concrete Properties			Compressive strength (MPa)			
	Slump (mm)	Air (%)	Density (kg/m^3)	3-d	7-d	28-d	91-d
Ref	140	6.2	2255	29	35	48	49
MS-075	160	1.8	2364	32	42	55	62
MS-100	150	1.7	2372	38	47	59	63

Concrete Properties (inch-pound)

Mixture	Fresh Concrete Properties			Compressive strength (psi)			
	Slump (in.)	Air (%)	Density (lb/yd^3)	3-d	7-d	28-d	91-d
Ref	5.5	6.2	3810	4205	5075	6969	7105
MS-075	6.3	1.8	3995	4640	6090	7975	8990
MS-100	5.9	1.7	4008	5510	6815	8555	9135

	Reference	MS-075	MS-100
Durability Factor, DF (%), after 300 cycles	105	101	103



ASTM C 666
Procedure A

$$\text{Durability Factor (DF)} = \frac{E_{300}}{E_0} \times 100\%$$

E_{300} = Modulus after 300 cycles

E_0 = Modulus before f/t tests

	Reference	MS-075	MS-100
Scaled mass loss (g/m^2) after 50 cycles	425	520	566
Visual rating after 50 cycles	2.5	2.5	2.5

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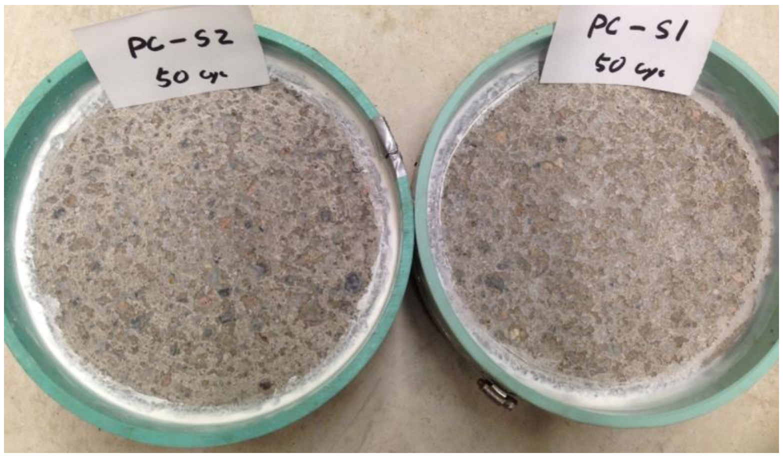
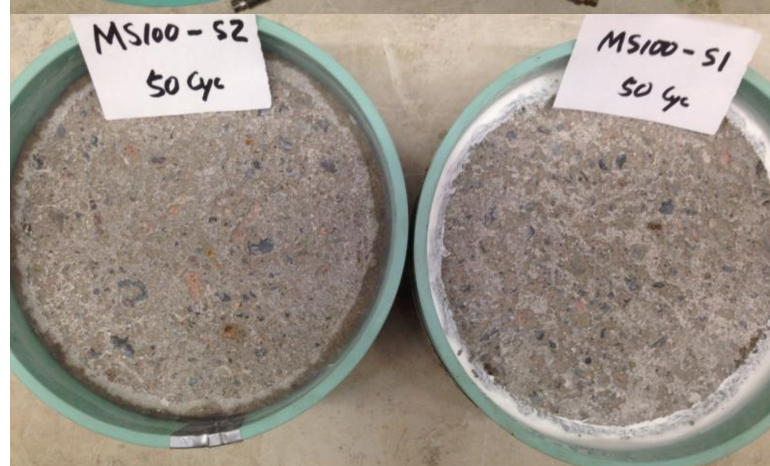




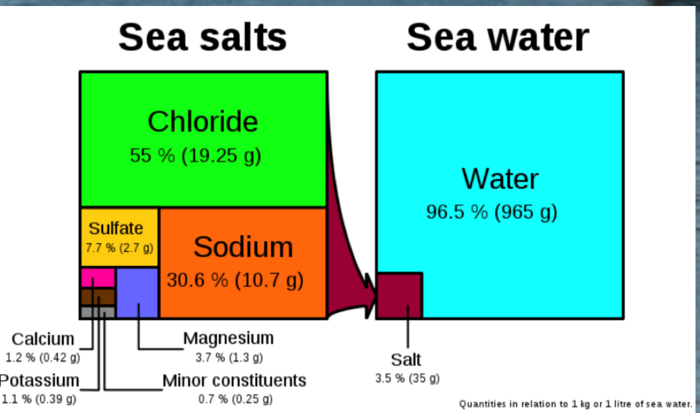
6% Air

- Slabs placed Fall 2013
- Photos taken Summer 2017
- 4 Winters

0.75% MS

1.00% MS

- Between 100 to 160 Freeze/Thaw Cycles per Annum
- Highest Tides in the World – up to 6.7 m (22 feet)
- 19,300 ppm chloride (3.52% salinity)
- Established in 1936 by USACE to study concrete for the Passamaquoddy Tidal Power Project (3 billion kWh/y)



Mid-Tide Wharf

- Photo taken in Sept 2017
- Beams placed in Summer 2014


SECTION 112 - 2006
PERMEABLE CONCRETE BASE
R3


Photo – August 2007
Pervious Concrete – placed 2006


CM 1
3
5
INCH
1
2
3

Performance of Concrete at Treat Island

LW Concrete with Polystyrene Spheres (no Air)

Control (6% air)

Performance of Concrete at Treat Island

LW Concrete with Polystyrene Spheres (no Air)

Control (6% air)

LWA Concrete Slabs cut from Nickel Bridge after 30+ Years

- Slabs placed at mid-tide level in August 2008

LWA Concrete Slabs cut from Nickel Bridge after 30+ Years

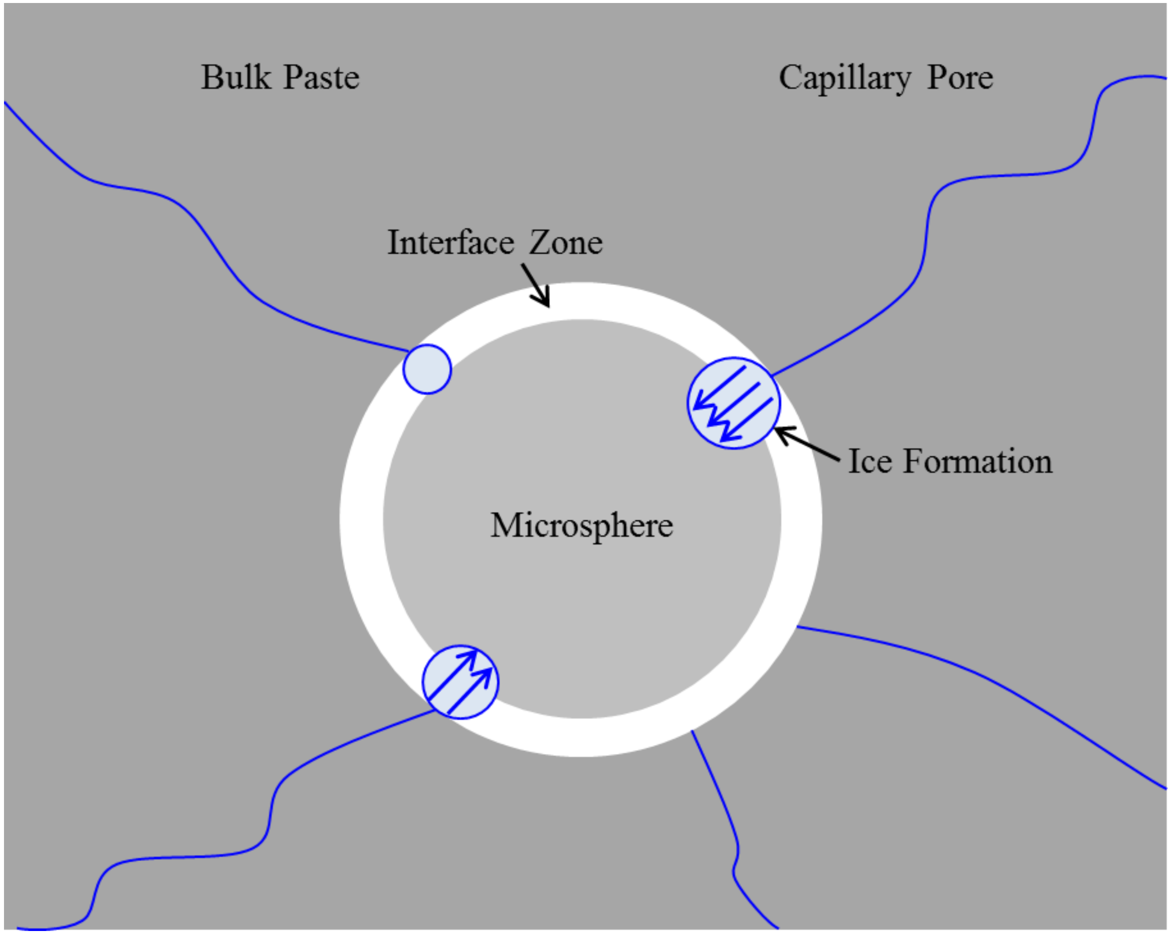
- Photo – June 2015

Mechanism of Frost Protection

Ong et al (2015): ACI Materials J.

Hypothesis:

- "Because the microspheres are polymeric, water impermeable, and compressible, the interfacial zone between the microsphere and mortar is believed to act as a "void" in which ice can form, due to the weak binding between the polymeric microsphere and the cement paste and the much higher CTE of the polymeric shell"



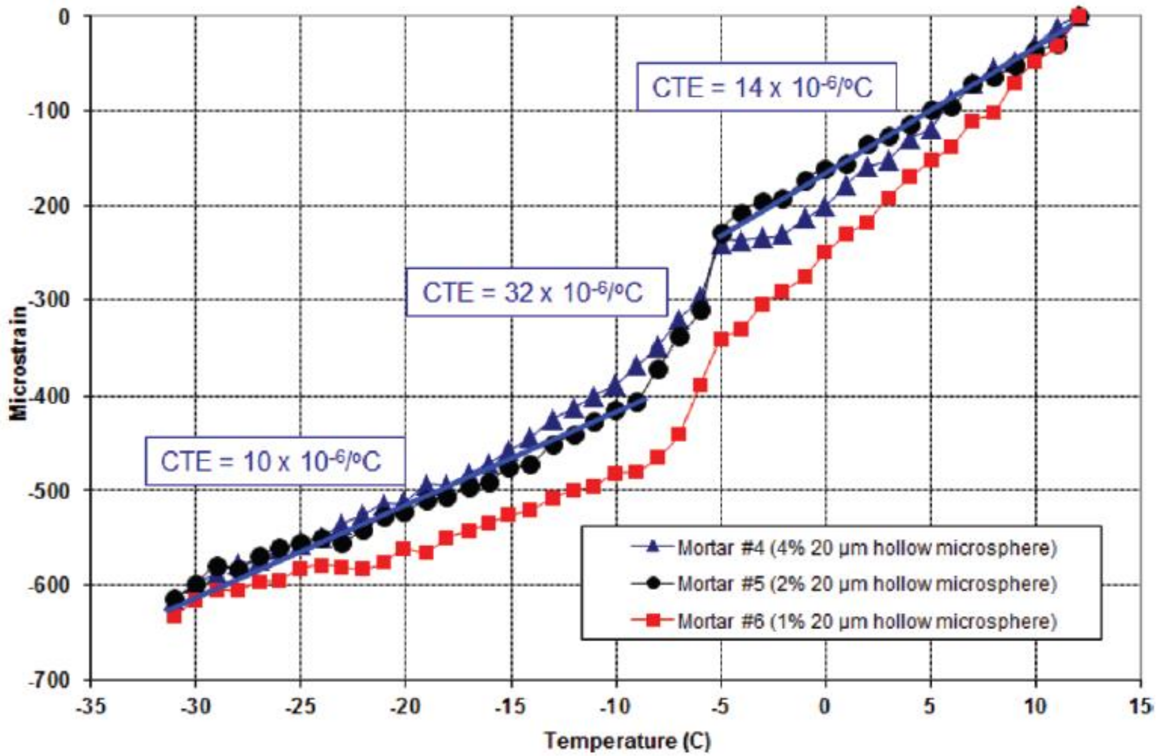
CTE Microspheres 100 to 200 x 10^{-6}/°C

Mechanism of Frost Protection (contd.)

Ong et al (2015): ACI Materials J.

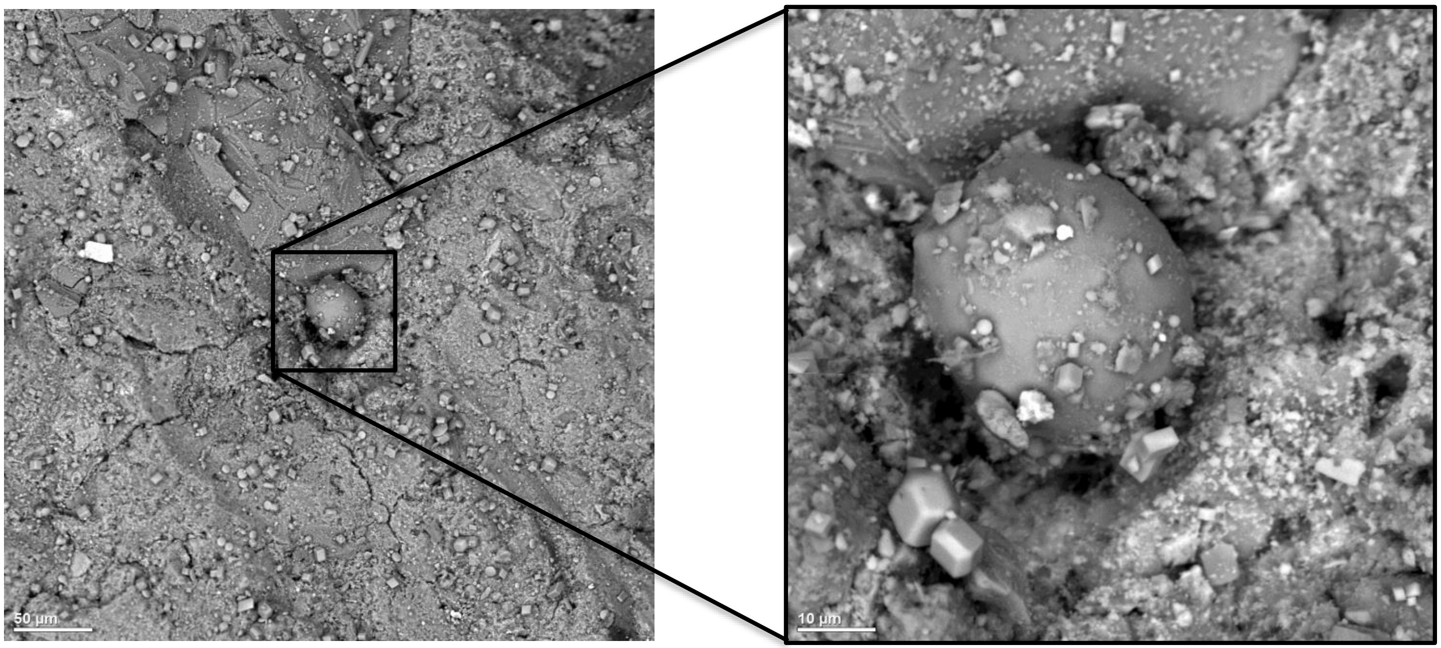
Hypothesis:

- "Ice forms during freezing at the interfacial zone between the microsphere and the mortar.
- As the number of interfacial zones increases with an increase in the volume fraction of microspheres, resistance to freezing-and-thawing damage of the mortar is enhanced."



Microstrain as function of temperature during freezing for mortar containing 1, 2, or 4% by volume of 20 μm diameter hollow (compressible) microsphere during first cycle of testing.

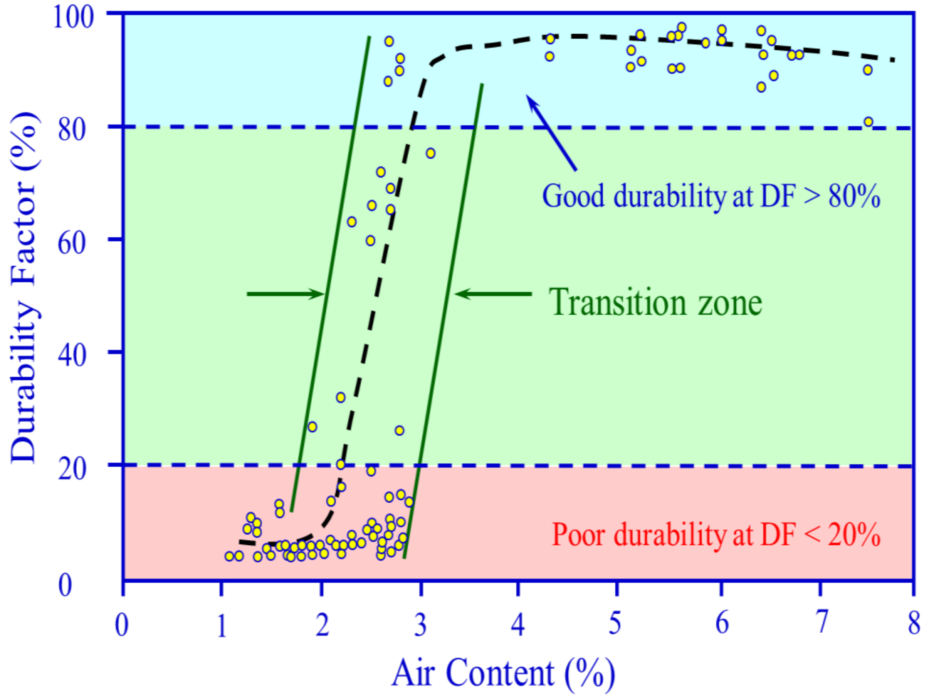
Mechanism of Frost Protection (contd.)



- Fracture surface of concrete (1% MS) saturated, frozen and viewed on cryostage in SEM

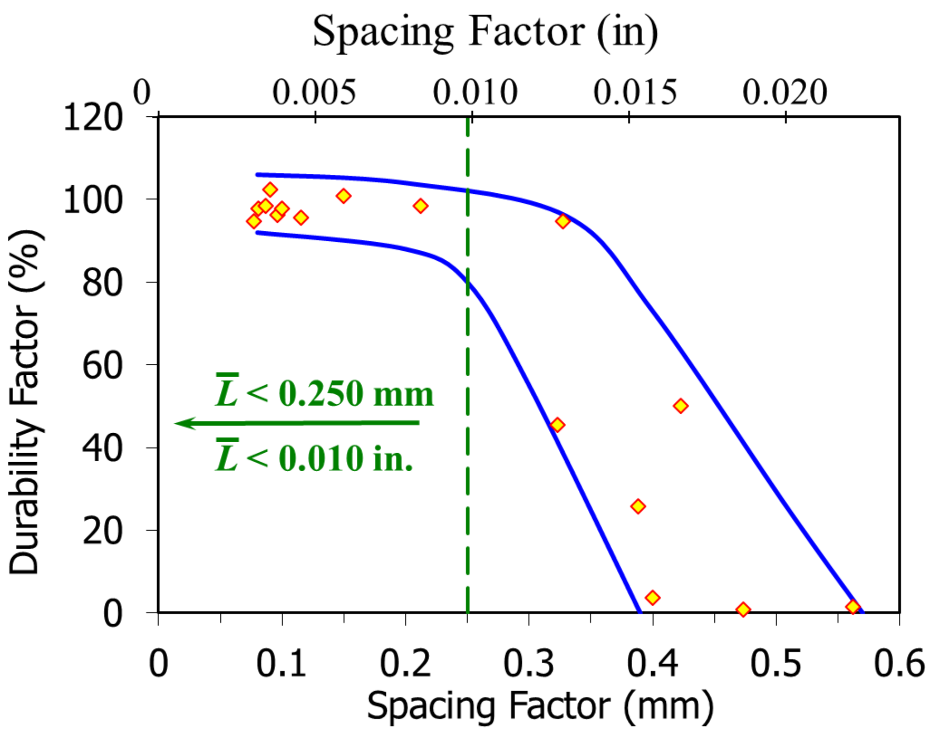
Air-Entrained Concrete

Effect of Air Content



From Newlon & Mitchell, 1994

Effect of Spacing Factor



Conclusions

- The incorporation of polymeric microspheres (MS) at 0.75% by volume provides resistance to cyclic freezing-and-thawing in the presence of deicing salts or in seawater.
- Concrete containing 0.75% or 1.00% MS (by volume) showed increased strength compared to concrete with the same proportions but with 6% entrained air.
- Evidence is presented to support the previously proposed mechanism that the interfacial zone between the microspheres and the cementitious matrix provides space to “accommodate freezing water and relieve hydraulic pressure” in much the same manner as do entrained air bubbles.