INNOVATIONS

COMPLIANCE CONCEPT IN PROTECTION OF CONCRETE FROM FREEZING-AND-THAWING DAMAGE

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aci CONCRETE CONVENTION

Use of Particles as an Alternative to Air Entrainment

- Air entrainment is effective for achieving a freezing-and-thawing durable concrete but difficult to control.
- There is interest to develop alternative technologies.
- Polymeric microspheres, as particles, have been found to protect concrete from freezing-and-thawing damage.
  - No detailed quantitative analysis reported on how the microspheres, or particles in general, provide protection.
  - All microspheres are not created equal; dosage requirements would depend on specific properties of the microspheres. It would be important to know what properties control performance when comparing test data on microspheres from different sources.
- *Goal of the study*: address the following questions through a detailed analysis to reveal factors that can impact performance and ensure consistency in the use of particles as an alternative to air entrainment.
  1. *What are the characteristics of particle types that can protect concrete from freezing-and-thawing damage?*
  2. *What quantity (or volume fraction) of a particle type is needed to achieve a freezing-and-thawing durable concrete?*

Key Concepts in the Analysis

- New concept of *particle compliance* with respect to freezing-and-thawing of concrete which establishes functional equivalence between particles and air voids.
- *Size of pore or void* as it relates to *temperature at freezing of water*, and to *tensile stresses induced by ice crystallization*.
- *Spacing* as it relates to *dispersion of air voids or particles*, and *protected paste volume* as it relates to *spatial distribution of air voids or particles*.
- *Compliance concept* combined with *spacing* and *protected paste volume concepts* to provide a *unified basis* for determining the quantity of air voids or particles needed to achieve a freezing-and-thawing durable concrete.

Particle Compliance

- ❑ How can particles without accessible inner spaces protect concrete from freezing-and-thawing damage as air voids do?

- ❑ By creating spaces through differential contraction between the particle and the surrounding cementitious matrix during temperature drops.
  - ➢ Particle types that can create such spaces for ice crystals to grow must have *thermal coefficient of expansion and contraction* greater than that of the surrounding cementitious paste and must not bond to the paste.

- ❑ A particle type with the same level of *volume change or compliance* as air voids would be expected to protect concrete from freezing-and-thawing damage.

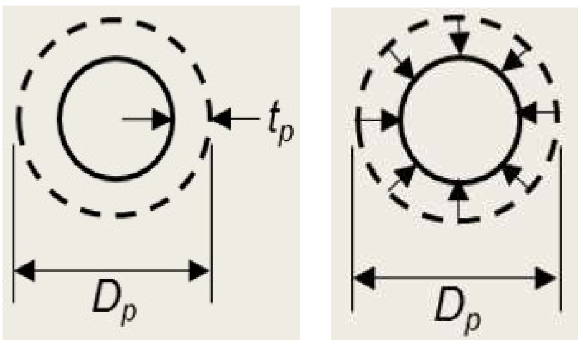
- ❑ *But can air voids be compliant?; that is, undergo elastic deformation or change in volume*? Yes, if it is assumed that *air voids act as particles*:
  - ➢ A *void-particle duality* of entrained air in concrete.
  - ➢ Air voids assumed to act as particles is consistent with the observation that the air voids have shells around them that are denser than the surrounding cementitious paste.

Quantification of Particle Compliance

- Thermal contraction of a particle during freezing creates a ring-shaped or annulus void. Also, thermal contraction of air in an air void would create a hypothetical annulus void around the "air-void particle".

- Need to quantify the *compliance* of a given particle type, as well as that of an "air-void particle", to relate the particle diameter to the air-void diameter.

$t_p << D_p$



- Creation of annulus void is visualized as mass of material m_p with thickness t_p pushing on the core of the particle.
- m_p/t_p represents stiffness of the particle, hence, $1/(m_p/t_p)$ represents particle compliance. (Stiffness is inversely proportional to thermal coefficient of volume expansion and contraction, c_{tp}.)
- $1/(m_p/t_p) \propto c_{tp}$
- Treating air voids as particles: $1/(m_a/t_a) \propto c_{ta}$
- Hence, the compliance of a particle type is equal to that of an air-void particle having the compliance value expressed by the right side of this equation:

$$\frac{1}{m_p/t_p} = \left(\frac{1}{m_a/t_a}\right)\left(\frac{c_{tp}}{c_{ta}}\right)$$

Compliance ratio: links particle diameter (D_p) to air-void diameter at 1 atm. (D_a):

$$C_f = \frac{(m_a/t_a)/\rho_a}{(m_p/t_p)/\rho_p} = \left(\frac{c_{tp}}{c_{ta}}\right)\left(\frac{\rho_p}{\rho_a}\right) \Longrightarrow D_p = D_a\sqrt{\left(\frac{c_{ta}}{c_{tp}}\right)\left(\frac{\rho_a}{\rho_p}\right)} = D_a\sqrt{\frac{1}{C_f}}$$

Functional Equivalence between Particles and Air Voids

- *Effective diameter* (D_e) for a particle type is the minimum diameter of air-void particles with the same compliance as the particle type:

$$D_e = D_a \sqrt{\left(\frac{c_{ta}}{c_{tp}}\right)\left(\frac{\rho_a}{\rho_{ef}}\right)} = D_a \sqrt{\frac{\rho_a}{\rho_{ve}}} = D_a \sqrt{\frac{1}{C_{ef}}} \Rightarrow$$

Particles of a given type can be treated as entrained air voids at a minimum or effective diameter D_e. (That is, there is functional equivalence between a particle type and air voids at a minimum diameter D_e.)

- D_e is obtained by considering the following:
  - The nucleation of ice in typical large-size structures in the field has been estimated to occur at a temperature (T_f) of -1°C.
  - For freezing at $T_f = -1$°C, the sizes of the annulus voids are: $t_p \geq$ 0.13 μm. $\left[T_f \propto \left(-\frac{1}{t_p}\right)\right]$
  - For t_p ≥ 0.13 μm, induced stresses, σ_i, due to ice crystallization are very low. $[\sigma_i \propto \frac{1}{t_p}]$
    - An adequate number of such annulus voids in non-air-entrained concrete would be expected to protect concrete from freezing-and-thawing damage at the same level as entrained air voids.
  - Based on the volume of the annulus void and the temperature at freezing, t_p is given by:

$$t_p = \frac{1}{12} c_{tp} D_p T_{amb} \left(1 + \sqrt{1 + \frac{k}{c_{tp} D_p T_{amb}^2}}\right) \Rightarrow$$

For a particle type with diameter D_p, this gives the size of the annulus void in which nucleation of ice would occur at a temperature ≤ -1°C.

Minimum Volume Fraction of Air Voids and Particles

- How do we relate the minimum volume fraction of air voids or particles (A_{min}) needed to achieve a freezing-and-thawing durable concrete to the size of the air voids or the particles?
  - By establishing criteria for *good dispersion* and *good spatial distribution* of the air voids or particles.
    - *Good dispersion*: ➡ air-void or particle <u>size and spacing are as small as possible</u>.
    - *Good distribution*: ➡ paste volume is homogeneously filled with air voids or particles for an <u>adequate volume of the paste to be protected</u>.
    - $A_{min} = \frac{pD_e}{8\bar{s}_{limit} - D_e}$ ➡ For air voids, and for various particle types if the size of the annulus void, t_p, is sufficiently large.

Accounting for t_p :

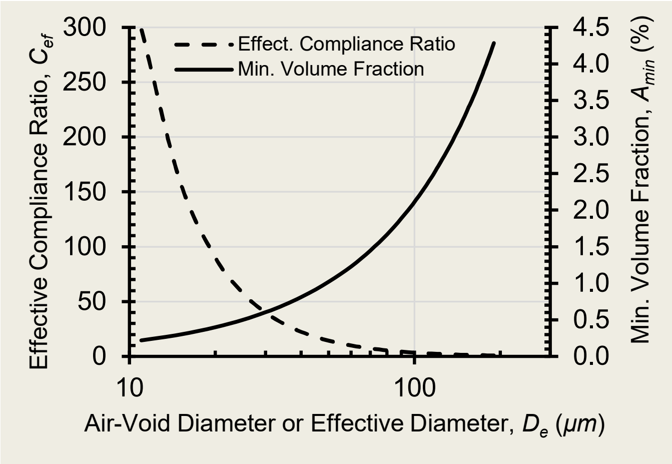
- If $D_p \le D_e$: $A_{min} = \left(\frac{pD_e}{8\bar{s}_{limit} - D_e}\right)\left(\frac{0.13}{t_p}\right)$
- If $D_p > D_e$: $A_{min} = \left(\frac{pD_p}{8\bar{s}_{limit} - D_p}\right)\left(\frac{0.13}{t_p}\right)$

where $0.13/t_p = 1$ for $t_p \ge 0.13$ μm

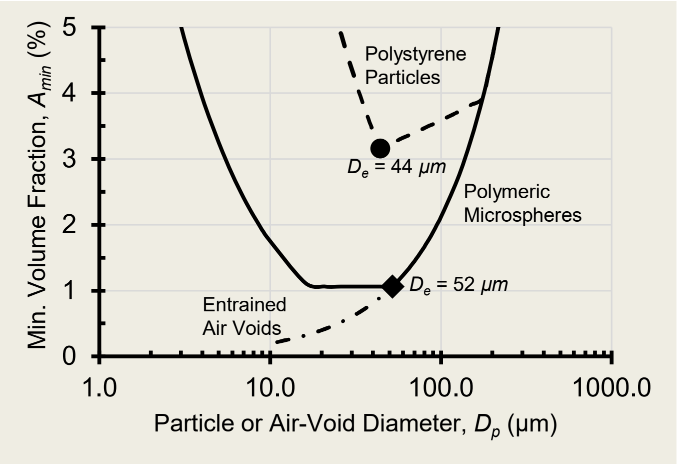
Minimum Volume Fraction of Air Voids and Particles

(Illustrate use of the equations.)

Paste content p = 0.30

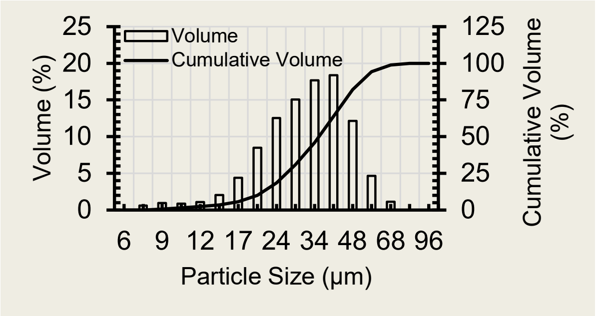


Paste content p = 0.30



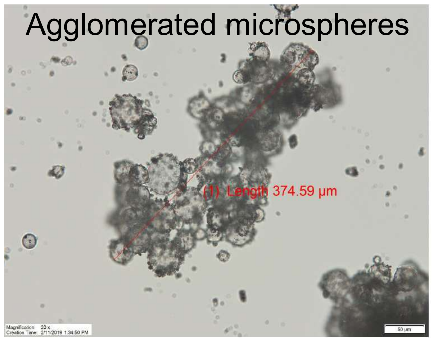
Particle size distribution

- Use D_{50} in place of D_p to calculate A_{min}



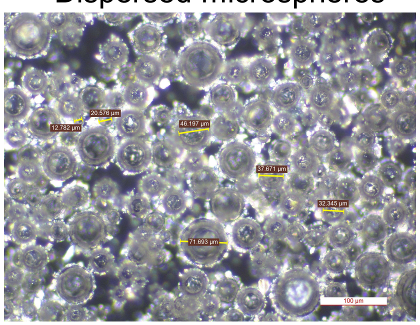
Freezing-and-Thawing Test Data

- Polymeric microspheres.



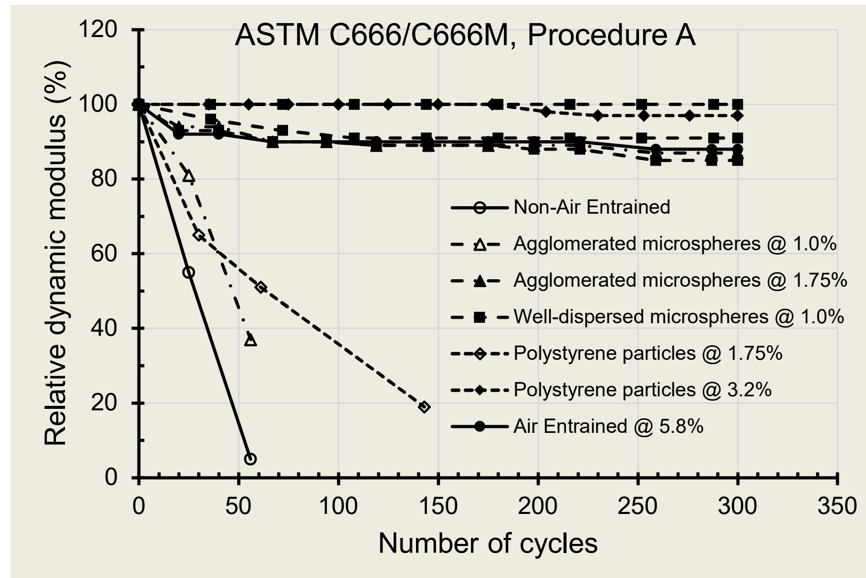
Need to eliminate microsphere agglomeration to achieve consistent performance in protecting concrete at a minimum fixed dosage.

Dispersed microspheres



Microspheres are well-dispersed when blended with mineral powder.

- Polystyrene plastic particles obtained from cryogenic grinding.



Freezing-and-thawing test data confirm the results of the compliance-based analysis.

Steps for Calculating Minimum Volume Fraction (A_{min}) for any Particle Type

1. Determine the average size of the particles as the D_{50} size obtained from a particle size distribution.

2. Calculate the effective diameter D_e for the particle type:

$$D_e = D_a\sqrt{\left(\frac{c_{ta}}{c_{tp}}\right)\left(\frac{\rho_a}{\rho_{ef}}\right)} = D_a\sqrt{\frac{1}{C_{ef}}}$$

(Note: A_{min} is least if D_{50} = D_e)

3. Calculate the annulus void size t_p corresponding to D_{50}:

$$t_p = \frac{1}{12}c_{tp}D_{50}T_{amb}\left(1+\sqrt{1+\frac{k}{c_{tp}D_{50}T_{amb}^2}}\right)$$

4. Calculate the minimum volume fraction A_{min}:

- If $D_{50} \leq D_e$: $$A_{min} = \left(\frac{pD_e}{8\bar{s}_{limit} - D_e}\right)\left(\frac{0.13}{t_p}\right)$$
- If $D_{50} > D_e$: $$A_{min} = \left(\frac{pD_{50}}{8\bar{s}_{limit} - D_{50}}\right)\left(\frac{0.13}{t_p}\right)$$

where $0.13/t_p$ = 1 for $t_p \geq 0.13$ μm

INNOVATIONS

With the compliance-based equations, we can ask questions like the following in order to design and produce microspheres with enhanced efficiency, specifically for use in concrete:

If you could produce polymeric microspheres for use in concrete to achieve durability at a minimum microsphere content that corresponds to entrained air content of 0.30% by volume of concrete, what should be the *average diameter* and *density* of the microspheres, given the following?

- Thermal coefficient of volume expansion and contraction of the microspheres is 2180 x 10^{-6}/℃
- Maximum microsphere spacing to achieve durable concrete is 0.19 mm (0.008 in.)
- Use 30% as a typical paste content of concrete

- *Consider this a practice question in the use of the compliance-based equations*.

Thank You!

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Backup Slides

Values for Some Key Parameters

- From previous published research, maximum spacing of air voids (or particles) is: $\bar{s}_{limit}$ = 0.19 mm (0.008 in.) (Conservative value to use for all grades of concrete.)

- Per Powers' observation, average diameter (D_a) of entrained air voids in concrete (under ambient condition of one atmosphere pressure) is taken to be equal to the maximum spacing ($\bar{s}_{limit}$): D_a = 190 μm (0.19 mm)

- Density of air under one atmosphere pressure: ρ_a = 1.2 kg/m^3

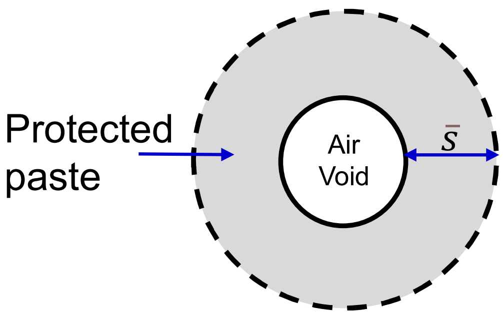
- Ambient temperature, T_{amb} = 20℃

- Thermal coefficient of volume expansion and contraction of air at 20℃: c_{ta} = 3400 x 10^{-6}/℃

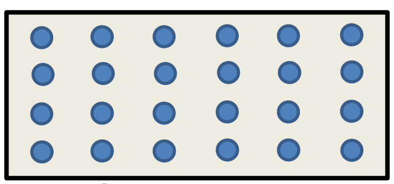
- Effective density for a particle type: $\rho_{ef} = \begin{cases} \rho_p \ \ for\, \rho_p \le 360\, kg/m^3 \\ 360\, kg/m^3 \ \ for\, \rho_p > 360\, kg/m^3 \end{cases}$

Air-Void Dispersion and Spatial Distribution

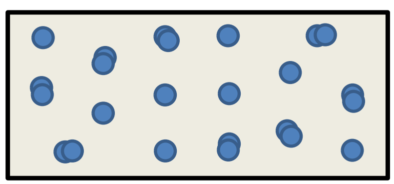
(Brief review of air-void system.)



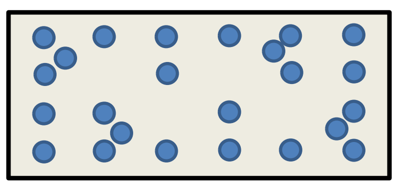
- During freezing, water is drained into the air void from the zone around it.
- The size of the zone or mean spacing ($\bar{s}$) is the flow length, quantified by Powers as *spacing factor*.
- The volume of paste within the zone was considered by Philleo as the *protected paste volume*.
- For the air voids to be highly efficient, Powers observed that the air-void spacing and diameter must be of the same order of magnitude and must be as small as possible:
  - ➢ Air voids must be uniformly dispersed (not agglomerate and coalesce).
- For a large volume of the paste to be protected, the paste volume must be homogeneously filled with the air voids (that is, the air content must be adequate for the given paste content):
  - ➢ Air voids must be evenly distributed (not cluster).



Good dispersion
Good distribution



Poor dispersion
Good distribution



Good dispersion
Poor distribution

Dispersion and distribution concepts are applicable to particles as well.

$$\bar{s} = 2F\frac{p^2}{\alpha A}$$

($\bar{s}$ quantifies dispersion)

$$F = \frac{8}{p/A\ +\ 1} \leq 1$$

(For comparing systems with a fixed void-size distribution.)

$$F = \frac{8\left(\frac{\alpha}{\alpha_1}\right)}{p/A\ +\ 1} \leq 1$$

(For comparing systems with different void-size distributions.)

(The protected paste volume fraction, F, quantifies spatial distribution)

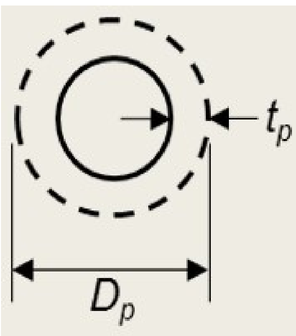
Functional Equivalence between Particles and Air Voids

- For air voids as particles with density (ρ_v) equal to the density (ρ_p) of the particle type, the diameter D_v is:

$$D_p = D_a\sqrt{\left(\frac{c_{ta}}{c_{tp}}\right)\left(\frac{\rho_a}{\rho_p}\right)} \Rightarrow D_v = D_a\sqrt{\frac{\rho_a}{\rho_v}}$$

- To achieve *equal compliance* of the particle type and air-void particles based on these equations, what criteria must be established?
  ⇒ *Criteria relate to the size of the particle and the size of the annulus void.*

$t_p << D_p$



- The size of the annulus void (t_p) must be such that induced stress, $\sigma_i << \sigma_t$ $\quad [\sigma_i \propto \frac{1}{t_p}]$
- For freezing at $T_f = -1℃$, $t_p \geq 0.13$ µm $\quad \left[T_f \propto \left(-\frac{1}{t_p}\right)\right]$

($t_p \geq 0.13$ µm ⇒ induced stresses, σ_i, due to ice crystallization are very low.)

$$t_p = \frac{1}{12}c_{tp}D_pT_{amb}\left(1+\sqrt{1+\frac{k}{c_{tp}D_pT_{amb}^2}}\right) \qquad t_a = \frac{1}{12}c_{ta}D_vT_{amb}\left(1+\sqrt{1+\frac{k}{c_{ta}D_vT_{amb}^2}}\right) \geq 0.13\ \mu\text{m}$$

$D_v \geq 11\ \mu m$ ⇒ 11 µm is diameter of smallest air void in which nucleation of ice would occur at a temperature of -1℃ to achieve a durable concrete.

Utilizing the D_v and D_p equations above with $D_v \geq 11\ \mu m$:

$$D_e = D_a\sqrt{\left(\frac{c_{ta}}{c_{tp}}\right)\left(\frac{\rho_a}{\rho_{ef}}\right)} = D_a\sqrt{\frac{\rho_a}{\rho_{ve}}} = D_a\sqrt{\frac{1}{C_{ef}}}$$

⇒ Particles of a given type can be treated as entrained air voids at a minimum or effective diameter D_e.

Minimum Volume Fraction of Air Voids and Particles

- How do we relate the minimum volume fraction of air voids or particles (A_{min}) needed to achieve a freezing-and-thawing durable concrete to the size of the air voids or the particles?
  - By establishing criteria for *good dispersion* and *good spatial distribution* of the air voids or particles.
    - *Good dispersion*: ➡ air-void or particle size and spacing are as small as possible.
    - *Good distribution*: ➡ paste volume is homogeneously filled with air voids or particles for a large volume of the paste to be protected.
    - Air-void spacing equation: $\bar{s} = 2F\frac{p^2}{\alpha A}$
    - Protected paste volume fraction: $F = \frac{8}{p/A + 1}$
    - The parameter αA is the total surface area of the air voids in a unit volume of concrete. ➡ $(\alpha A)_{min}$ for durable concrete.
      - $\alpha A \geq (\alpha A)_{min}$ is a condition for *good dispersion* of the air voids.
      - $F \geq F_{min}$ is a condition for *good distribution* of the air voids. $F_{min} = \frac{D_e}{\bar{s}_{limit}} \leq 1$: substitute into F eq'n. to obtain A_{min}.
    - $A_{min} = \frac{pD_e}{8\bar{s}_{limit} - D_e}$ ➡ For air voids, and for various particle types if the size of the annulus void, t_p, is sufficiently large.

Accounting for t_p :

- If $D_p \leq D_e$: $A_{min} = \left(\frac{pD_e}{8\bar{s}_{limit} - D_e}\right)\left(\frac{0.13}{t_p}\right)$
- If $D_p > D_e$: $A_{min} = \left(\frac{pD_p}{8\bar{s}_{limit} - D_p}\right)\left(\frac{0.13}{t_p}\right)$

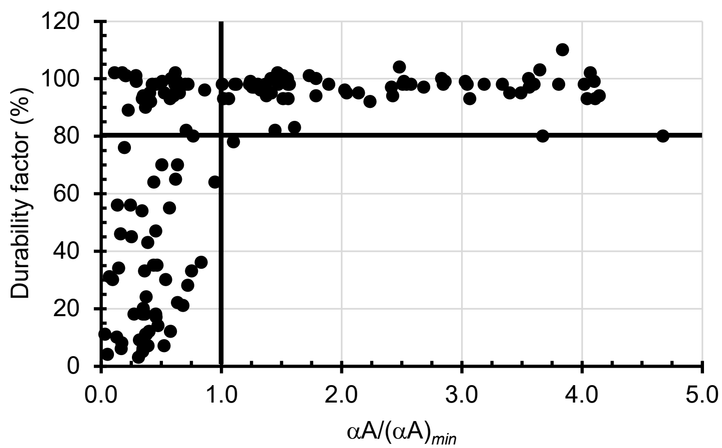
where $0.13/t_p$ = 1 for $t_p \geq 0.13$ μm

Condition for Good Dispersion of Air Voids or Particles

- Minimum total surface area of air voids or particles per unit volume of concrete:

$$(\alpha A)_{min} = \left(\frac{2}{\bar{s}_{limit}}\right)p^2$$

- Example: Assessment of freezing-and-thawing durability based on total surface area of air voids per unit volume of concrete (αA) obtained from air-void analysis of hardened concrete:

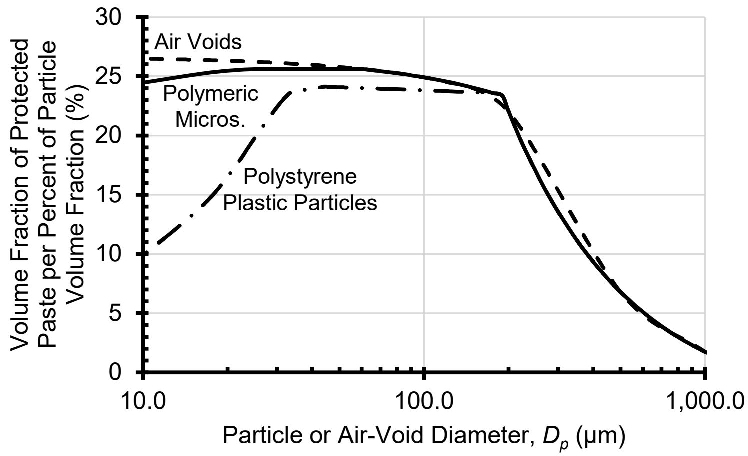


- 100% of concretes with $\alpha A \geq (\alpha A)_{min}$ had excellent durability: Durability Factors ≥ 80%. (No false positives.)
- 65% of concretes with $\alpha A < (\alpha A)_{min}$ had Durability Factors < 80%. (Only 35% false negatives.)
- $\alpha A/(\alpha A)_{min}$ is a good predictor of durability potential of concrete.

• Cyclic freezing-and-thawing test per ASTM C666/C666M, Procedure A.

Particle or Air-Void Efficiency

- Efficiency is rated as:
  - volume fraction of protected paste per percent of particle or air-void volume fraction = F/A_{min}



- The gas-filled polymeric microspheres are as efficient as air voids down to a size of about 20 μm, and are more efficient than plastic particles, such as polystyrene particles, for sizes < 200 μm.

- Efficiency is slightly higher when the particles have a distribution in sizes than when they are single sized. A distribution in sizes is quantified by the spread of the distribution, which for a gamma function distribution is given by the value of β. When the particles have a distribution in sizes, β > 0, whereas the particles are single sized when β ≈ 0.
  - At a constant volume fraction of particles (A), a slightly higher efficiency is indicated by a slightly larger value of the protected paste volume fraction, F, when β > 0:

$$F = \frac{\left(\frac{18}{\pi}\right)\left(\frac{5}{4} + \frac{\beta\alpha}{8}\right)}{p/A + 1} \leq 1$$

Minimum Volume Fraction of Non-Spherical Particles

- The compliance-based analysis assumes the particles are spherical.
  - Particle size distributions obtained from methods such as laser diffraction yield measures of average diameter (e.g., D_{50}) based on equivalent spherical diameter of the particles. Therefore, D_{50} can be used in the equations.
- In general, the total surface area of particles in a unit volume of concrete, αA, determines if there is an adequate number of particles to ensure a durable concrete.
  - For equivalent spherical particles to represent non-spherical particles in a unit volume of the concrete, set the surface area of the equivalent spherical particle (with diameter D_s) to the surface area of the non-spherical particle. This yields the diameter of the equivalent spherical particle, D_s, to use in the compliance-based equations.
- Examples: single-size filament particles, such as polypropylene fibers, of cross-sectional diameter D_f and length l_f; equal surface areas yield:

$$D_s = D_f \sqrt{\frac{l_f}{D_f}}$$

  - Polypropylene microfiber with a typical diameter of 13 μm and a length of 13 mm.
    - D_s = 410 μm > D_e = 35 μm; $\Rightarrow$ A_{min} ~ 10%. At such a volume fraction of microfiber, the concrete would be unworkable.
  - Polypropylene macrofiber with a typical diameter of 0.5 mm and a length of 50 mm.
    - D_s = 5000 μm > D_e = 35 μm; $\Rightarrow$ A_{min} is extremely large and unrealistic.
  - Therefore, the typical polypropylene microfibers and macrofibers used in concrete cannot provide protection from freezing-and-thawing damage because they are too large.