A New Way to Deliver Protection from Freezing-and-Thawing Damage

Blending microspheres with mineral powder minimizes agglomeration and ensures durability

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by Emmanuel K. Attiogbe

Air entrainment has long been known as an effective means for protecting concrete from cyclic freezing-and-thawing (F-T) damage; air voids in the matrix provide spaces for ice crystals to grow and thereby relieve internal tensile stresses that can cause cracking of the concrete. Air bubbles are entrained in fresh concrete by the mechanical action of mixing the ingredients, and they are stabilized by using a surfactant, known in the industry as an air-entraining agent (AEA). However, the amount of stable air that is entrained can be controlled only indirectly through the adjustment of the amount or type of AEA added to the concrete. Further, researchers have found that AEAs may not be effective if they do not support the generation of a consistent spacing of air voids in the concrete. Many producers encounter difficulties in achieving consistent void spacing because the effectiveness of surfactants is affected by the ambient environment and the mixture constituents. Hence, it is desirable to have an alternative to air entrainment in which void structures are incorporated into concrete without requiring air bubbles to be stabilized during mixing. This has led to the development of technologies such as those that comprise hollow-core polymeric microspheres.[1-5]

A recent study provides a micromechanics-based explanation of how such microspheres protect concrete from F-T damage.[6] Commercially available hollow-core microspheres have polymeric walls and inner spaces filled with a liquid or a gas. The polymer shell and the filler materials have high rates of thermal expansion and contraction, enabling the microspheres to contract relative to the concrete during temperature drops. This differential contraction creates a spherical void between the microsphere and the concrete surface that was formed by the microsphere when the concrete set.

One type of microsphere known to protect concrete from damage due to cyclic F-T is trademarked Expancel®. This product is available in two forms:

- Gas-filled, wet-expanded microspheres in a wet foam or slurry form; or
- Gas-filled, dry-expanded microspheres in dry powder form.

In both forms, the microspheres have low densities, and they tend to adhere to each other and form agglomerations. This particle agglomeration is detrimental to performance because the microspheres must be uniformly dispersed throughout the concrete to protect the concrete from damage during cyclic F-T. Further, microspheres supplied as dry powder are difficult to handle, as the dry powder causes dusting. While the latter issue implies that the wet-expanded microspheres in slurry form would be preferred for use in concrete, the slurry creates challenges in concrete production because the very low-density microspheres segregate from the liquid medium during storage. To overcome this inherent instability, the slurry is best produced at the point of addition into the concrete.[3] This leads to high production and logistics costs that have stifled the introduction of the microsphere technology into general practice.

This article presents test data that show the effectiveness of a new method of delivery of microspheres into concrete. The new method is based on a microsphere-powder blend that eliminates or minimizes particle agglomeration and eases handling and delivery of the microspheres into concrete mixtures. Test data are provided to show the effectiveness of the delivered microspheres in protecting concrete from damage in standard tests for durability per ASTM C666/C666M, “Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing,” and ASTM C672/C672M, “Standard Test Method for Scaling Resistance of Concrete Surfaces

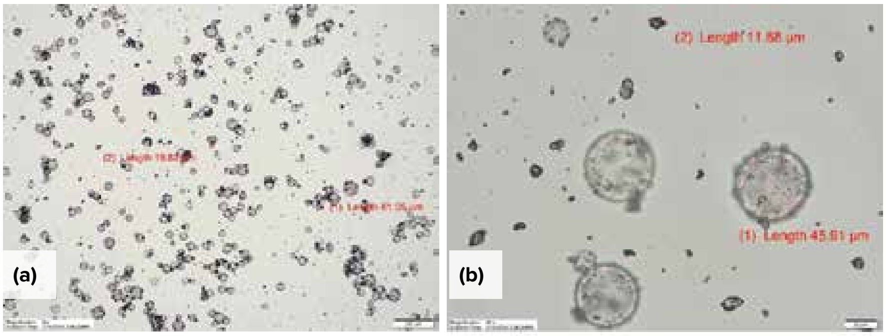

Fig. 1: Photomicrographs showing well-dispersed mineral-blended polymeric microspheres with an average particle size of 40 µm (0.0016 in.) and a density of 25 kg/m^3 (1.56 lb/ft^3): (a) at 5× magnification; and (b) at 40× magnification

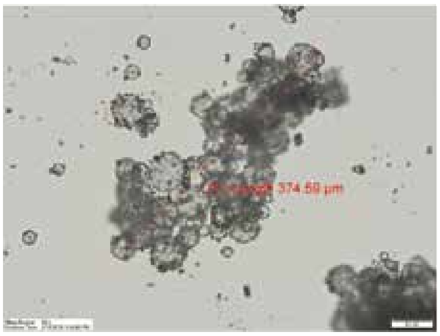

Fig. 2: Photomicrograph of agglomerations of polymeric microspheres at 20× magnification. Agglomerations occur when little or no mineral powder is present

Exposed to Deicing Chemicals." The effectiveness of the microsphere-powder blend is also compared to the effectiveness of conventional air entrainment produced with commonly available AEAs.

Mineral-Blended Polymeric Microspheres

Blending dry-expanded polymeric microspheres with an adequate quantity of mineral powder enables the surfaces of the microspheres to be coated. The coating prevents the microspheres from sticking together and agglomerating to form larger particles prior to being added to a concrete mixture and facilitates uniform dispersion of the microspheres into a concrete mixture. Also, for ease of handling, the microsphere-powder blend can be dispensed into the concrete mixture in a sack that disintegrates and disappears during mixing, thus avoiding the problem of dusting. Application of the microsphere-powder blend in concrete to provide protection from damage due to cyclic F-T is covered by U.S. Patent No. 10,730,794 B1.[7]

Photomicrographs of the microsphere-powder blend from optical microscopy are shown in Fig. 1. The photomicrographs show that the spherical microspheres are quite well dispersed in the powder blend. When no or an insufficient quantity of the mineral powder is blended with the microspheres, the microsphere particles are severely agglomerated, as shown in the photomicrograph in Fig. 2. The size labels on the photomicrographs represent the sizes for selected microspheres and mineral powder particles. As explained from the analysis in Reference 6, the quantity of agglomerated microspheres, either in dry powder or slurry form, by volume of concrete needed to achieve a durable concrete would be higher compared to that of the nonagglomerated, well-dispersed microspheres. Figure 3 is a photomicrograph obtained in cross-polarized light showing well-dispersed spherical microspheres with mineral powder adhering to them. When the microsphere-powder blend is mixed in concrete, the mineral powder is dispersed because its electrostatic attraction to the microspheres is broken.

The patented microsphere-powder blend is formulated to reliably protect concrete from damage at a fixed volume fraction in typical concretes. The powder blend formulation represented by the photomicrographs in Fig. 1 and 3 has a consistent particle size distribution. The quantity of mineral powder used in the formulation ensures that agglomeration is sufficiently reduced while also ensuring a sufficient quantity of microspheres to deliver the intended performance without using an excessive dosage of the powder blend in the concrete.

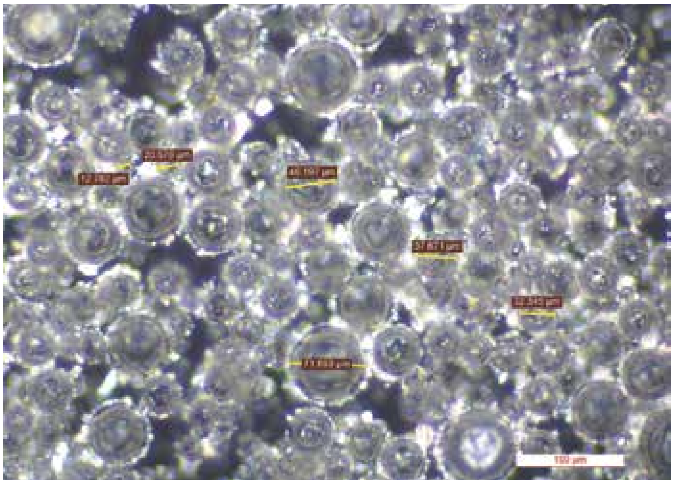

Fig. 3: Photomicrograph of mineral-blended polymeric microspheres in cross-polarized light at 200× magnification, showing adherence of the mineral powder particles on well-dispersed microspheres

Test Program

Three mixture categories were prepared (Table 1):

- Category A mixtures comprised basic constituents of aggregate, water, and cement;
- Category B mixtures comprised the same basic constituents as Category A, plus a commonly used AEA (surfactant); and
- Category C mixtures comprised the same basic constituents as Category A, plus mineral-blended microspheres.

Within each category, mixtures were prepared with a water-cement ratio (*w/c*) of either 0.52 or 0.42 (Table 1) using a rotary drum mixer. For all but one mixture in Category B, a

Table 1:
Concrete mixture proportions, slump, air content, and density

Constituents and properties	Concrete mixtures						
	A1	B1	C1	C2	A2	B2	C3
Cement, kg/m^3	335				400		
Coarse aggregate, kg/m^3	1104	1042	1104	1104	1068	1009	1068
Fine aggregate, kg/m^3	739	695	707	699	736	692	704
Water, kg/m^3	174				168		
w/c	0.52				0.42		
AEA, mL/m^3	—	96.2	—	—	—	230.8	—
Microsphere content, vol. % of concrete	—	—	1.0	1.25	—	—	1.0
HRWRA (Type F), mL/m^3	923	—	1235	1104	2762	962	2623
Slump, mm	155	140	140	140	115	135	110
Air content, vol. % of concrete	2.3	5.8	2.7	2.2	2.1	5.9	2.6
Density, kg/m^3	2336	2248	2314	2307	2375	2277	2320

Note: 1 kg/m^3 = 1.7 lb/yd^3; 1 mL/m^3 = 0.026 fl oz/yd^3; 1 mm = 0.04 in.

Type F high-range water-reducing admixture (HRWRA) was used to achieve a 125 to 180 mm (5 to 7 in.) target slump.

Category B mixtures were prepared with a commercially available Vinsol® resin-based AEA at a dosage needed to achieve an air content of about 6%. Category C mixtures were prepared with a mineral-blended microsphere powder added with the cement. Category C mixture proportions were based on the proportions of Category A mixtures, with the fine aggregate volume reduced to compensate for the volume of the added powder blend.

The microsphere-powder blend used to prepare Category C mixtures had a specific gravity of 0.25. Two powder blend dosages were used: 1.2 and 1.5% by volume of the concrete. These dosages were designed to yield microsphere dosages of 1.0 and 1.25% by volume of the concrete, respectively. These values were selected because the minimum volume fraction of microspheres in concrete needed to achieve durability against cyclic F-T is about 1.0%.[6]

The microsphere-powder blend for Mixture C3 was dispensed into the concrete mixture in a sack that disintegrated and disappeared during mixing. This sack was made of patented white paper that disintegrates more easily than typical paper sacks that have a high lignin or "glue" content.[8]

Basic tests

For each batch of concrete, unit weight and air content were measured per ASTM C138/C138M, "Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete," and ASTM C231/C231M, "Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method," respectively (refer to Table 1 for results). Also, three 100 x 200 mm (4 x 8 in.) cylinders were cast for compressive strength testing at 28 days per ASTM C39/C39M, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens."

Durability tests

Also for each batch of concrete, three 75 x 100 x 405 mm (3 x 4 x 16 in.) specimens were cast for testing in accordance with ASTM C666/C666M, Procedure A, and further, the mixtures with *w/c* of 0.42 were tested for salt scaling in accordance with ASTM C672/C672M, using two 300 x 300 x 100 mm (12 x 12 x 4 in.) specimens for each batch.

Evaluation of quality assurance test methods

In a separate study, concrete mixtures with microsphere volume fractions in the range of 0 to 2% were tested to determine if standard quality assurance test methods could be used to verify microsphere content in the field. The methods were:

- ASTM C173/C173M, "Standard Test Method for Air Content of Freshly Mixed Concrete by the Volumetric Method," modified only by omitting the addition of isopropyl alcohol[9]; and

Table 2:
Concrete strength and performance under repeated cycles of F-T

Test results	Concrete mixtures						
	A1	B1	C1	C2	A2	B2	C3
	w/c = 0.52				*w/c* = 0.42		
28-day compressive strength, MPa	37.3	33.9	36.6	35.4	51.4	41.8	45.7
Durability factor, % (≥ 60% at 300 cycles)	Fail	88	85	86	Fail	90	84
Relative durability factor, % (≥ 80% at 300 cycles)	—	100	97	98	—	100	93
Scaling rating at 50 cycles	—	—	—	—	5	1	1
Scaling mass loss at 50 cycles, g/m^2 (≤ 800 g/m^2 after 50 cycles)	—	—	—	—	901	123	65

Note: 1 kg/m^3 = 1.7 lb/yd^3; 1 mL/m^3 = 0.026 fl oz/yd^3; 1 mm = 0.04 in.; 1 MPa = 145 psi; 1 g/m^2 = 0.003 oz/ft^2

- The Super Air Meter (SAM) testing device,[10] applied in accordance with AASHTO TP 118, "Standard Method of Testing for Characterizing of the Air-Void System of Freshly Mixed Concrete by the Sequential Pressure Method."

The volumetric air content tests were performed under the assumption that the microspheres in a test sample would segregate from the concrete and conglomerate at the top of the graduated cylinder. The tests were conducted without the standard isopropyl alcohol because this chemical is a solvent that could cause the microspheres to collapse. The SAM investigation was performed under the assumption that the pressures used in the testing could compress the microspheres in the concrete mixture and enable the test to be sensitive to the microsphere content of the concrete.

Test Results and Discussion

The test data in Table 2 show that the compressive strength of Mixtures C1 and C3 with a microsphere content of 1.0% by volume of the concrete was about 10% higher than the strength of Mixtures B1 and B2 with about 6% air content. Therefore, from the standpoint of sustainability and cost benefits, concrete mixtures with the mineral-blended polymeric microspheres can have somewhat lower amounts of cementitious materials and yet match the strengths of mixtures with conventional AEAs.

Cyclic F-T

Per ASTM C666/MC666, Procedure A, for a concrete mixture to be considered able to withstand an F-T environment, it must achieve a durability factor of 60% or greater. Also, the durability factor of the concrete relative to that of an air-entrained concrete (that is, the relative durability factor) must be 80% or greater. The results show that concretes containing the microsphere-powder blend passed the cyclic F-T test at microsphere contents of 1.0 and 1.25%, with durability factor values within a narrow range of 84 to 86% (refer to Mixtures C in Table 2). Also, relative durability factor values in the range of 93 to 98% show that these concretes were comparable to the air-entrained concretes (Mixtures B). As expected, the non-air-entrained concretes (Mixtures A) failed the cyclic F-T test.

Figure 4 shows that the concretes containing the microsphere-powder blend and the air-entrained concretes passed the cyclic F-T test at relative dynamic modulus values

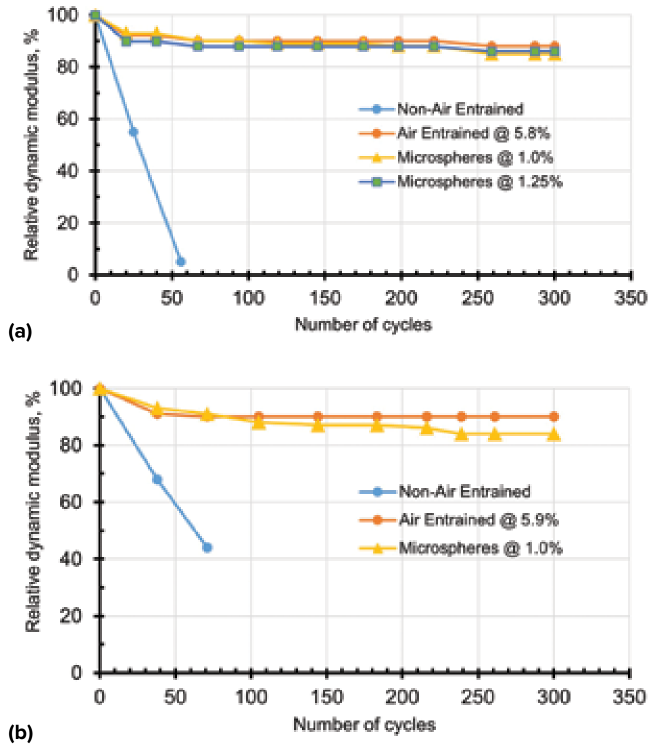

Fig. 4: Relative dynamic modulus versus number of cycles of F-T: (a) for Mixtures A1, B1, C1, and C2 with *w/c* = 0.52; and (b) for Mixtures A2, B2, and C3 with *w/c* = 0.42

that were quite stable from about 35 cycles to the end of the test, at 300 cycles of F-T. Microsphere contents of 1.0 and 1.25% yielded the same performance, as shown in Fig. 4(a), indicating that using more than the minimum microsphere content needed to achieve a durable concrete is not warranted. Figure 5 shows that for the concrete mixtures with a *w/c* of 0.42, the surface-scaling levels of Mixtures C (with microspheres) and Mixtures B (air-entrained) were comparable after the 300 cycles of rapid F-T in water.

Surface scaling

The visual surface-scaling ratings of the specimens evaluated for salt-scaling resistance (ASTM C672/C672M) as reported in Table 2 show that Mixture C3, containing the microsphere-powder blend, performed similarly to the air-entrained concrete (Mixture B2) with an average scaling rating of 1 (very slight scaling), compared to the scaling rating of 5 (severe scaling) for the non-air-entrained concrete (Mixture A2). The mass loss values were 65 g/m^2 (0.20 oz/ft^2) for Mixture C3 with microspheres, 123 g/m^2 (0.37 oz/ft^2) for Mixture B2 with air entrainment, and 901 g/m^2 (2.70 oz/ft^2) for Mixture A2 with no air entrainment. These values indicate acceptable performance for the microsphere concrete and the air-entrained concrete as per Canadian specifications that impose a limit of 800 g/m^2 (2.40 oz/ft^2) for mass loss after 50 cycles of F-T.[11]

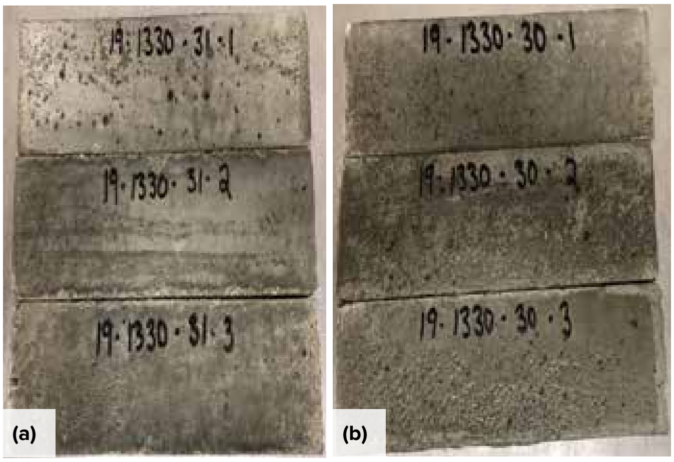

Fig. 5: Concrete specimens prepared with *w/c* = 0.42 shown after 300 cycles of rapid F-T per ASTM C666/C666M, Procedure A: (a) air-entrained concrete; and (b) microsphere concrete

Figure 6 shows the surface appearance of a test specimen containing microspheres compared to that of the non-air-entrained and air-entrained specimens after 50 cycles of testing. Superior performance is observed for the microsphere concrete and the air-entrained concrete compared to the severe scaling of the non-air-entrained concrete.

Microsphere dosing and quality assurance

As previously noted, the microsphere-powder blend was added to Mixture C3 in a sack designed to completely disintegrate and disappear during mixing. To dose a 0.76 m^3 (1 yd^3) batch of concrete, for example, one 20 L (0.71 ft^3) sack is required to be added to the mixture. Other sack sizes can be used as deemed appropriate. This method of dispensing the powder blend into a concrete mixture facilitates handling and eliminates any issue regarding dusting of the material. This method also facilitates adding the right quantity of the microsphere-powder blend by simply counting the number of sacks added instead of weighing the powder for every batch of concrete produced. In addition, tests of batches containing a range of dosages show that the modified ASTM C173/C173M test method can be used to verify the microsphere content of the concrete prior to concrete placement (Fig. 7). A layer of microspheres collects in the graduated neck of the volumetric meter beneath a small layer of foam. The thickness of the microsphere layer, in volume percent of the concrete, gives a measure of the microsphere content of the concrete. The preliminary evaluations conducted for this study showed that for a microsphere content of 1.0% by volume of concrete, the measured values were in the range of 1.0 ± 0.1%.

Tests conducted using the SAM testing device showed that non-air-entrained concrete mixtures with microspheres had similar SAM numbers as mixtures without microspheres. This

Fig. 6: Surfaces of concrete specimens prepared with *w/c* = 0.42 after 50 cycles of salt-scaling testing per ASTM C672/C672M: (a) non-air-entrained concrete; (b) air-entrained concrete; and (c) microsphere concrete

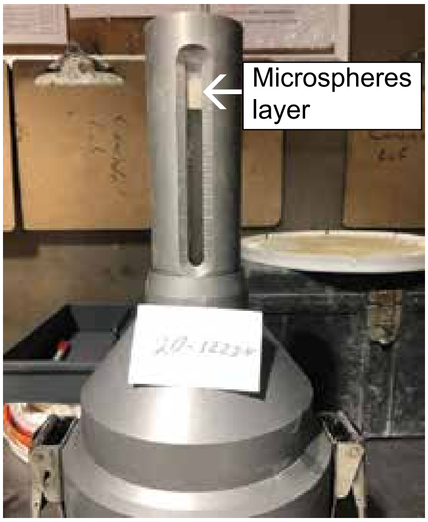

Fig. 7: The microsphere content of a concrete mixture can be evaluated using a volumetric meter

implies that the pressures used in the test are not high enough to compress the microspheres and yield readings that would vary with the microsphere content of the concrete. As such, the SAM testing would not be a suitable means of quality control for concrete containing microspheres. Carefully counting the number of sacks of the microsphere-powder blend added into a concrete batch, along with performing the ASTM C173/C173M test without using isopropyl alcohol, would verify that the microspheres are present in the right quantity prior to concrete placement.

Potential Benefits

Environmental benefits

The microsphere-powder blend, while eliminating the practical problems encountered in air entrainment, would also enable the large-scale use of fly ash with high unburned carbon content as a supplementary cementitious material.[9] Such low-grade fly ash is usually landfilled as it is considered unusable without further treatment because it makes air entrainment of concrete difficult or impossible. Also, use of the microsphere-powder blend to replace an equal volume of sand while achieving an F-T durable concrete would contribute to conservation of concrete sand as a natural resource.

Constructability benefits

Hard troweling of air-entrained concrete floors or slabs carries the risks of reduction in surface air content and delamination or blistering. Use of the microsphere-powder blend in place of air entrainment should allow for dense, polished, machine-troweled surfaces to be specified for concrete slabs in environments that could be at risk of exposure to cyclic F-T. Also, roller-compacted concrete and pervious concrete that are difficult to air entrain because of their stiff consistency[12,13] can be made durable against cyclic F-T with the addition of the microsphere-powder blend.

Recently, it has been shown that air bubbles dissolve in the fresh concrete when concrete is pumped but are reformed prior to hardening of the concrete.[14] As such, the air content of the hardened concrete would tend to be higher than the air content of the fresh concrete measured after pumping. This observation may also apply to wet-mix shotcrete, which is used in a variety of structural and repair applications.[15] Because the microsphere-powder blend will offer a more reliable and robust protection of pumped concrete from damage caused by F-T, it would eliminate the production and placement issues related to pumping of air-entrained concrete.

Concluding Remarks

The work reported here and in Reference 6 shows that precoating dry-expanded polymeric microspheres by blending with a mineral powder can minimize agglomeration of the microspheres and promote their uniform dispersion and distribution in a concrete mixture. The use of a disintegrating sack to dispense the material into a concrete mixture facilitates adding the right quantity of the microsphere-powder into a concrete batch simply by counting the number of sacks added instead of weighing the powder for every batch of concrete produced.

Cyclic F-T and deicing salt-scaling testing show that the microsphere-powder blend at a microsphere content of 1.0% by volume of the concrete is as effective as air entrainment in protecting concrete from F-T damage, but it is not saddled with the uncertainties associated with air entrainment. Performing the modified ASTM C173/C173M test without isopropyl alcohol would verify that the microspheres are present in the right quantity prior to concrete placement.

Also, as shown in Reference 6, the minimum quantity of microspheres by volume of concrete needed to protect the concrete from cyclic F-T is determined based on the required maximum spacing of the particles. As such, the spacing requirement is expected to be met when the minimum quantity of microspheres calculated from the equations in Reference 6 is used in the concrete. Therefore, microscopical analysis of the microsphere content and distribution in the hardened concrete based on ASTM C457/C457M, "Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete," would need to be developed. An appropriate range of magnification to use in the microscopical examination of the microsphere concrete would need to be established because the microspheres are much smaller than the typical size of entrained air voids. Preliminary evaluations of concretes containing microspheres using the current ASTM C457/C457M test method at higher magnifications than typically used, such as 200×, indicate that an acceptable level of accuracy would be achieved in quantifying the amounts of microspheres in the hardened concretes.

Acknowledgments

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Note: Additional information on the ASTM and AASHTO standards discussed in this article can be found at **www.astm.org** and **www.transportation.org**, respectively.

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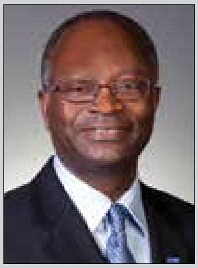

Emmanuel K. Attiogbe, FACI, is a Research Engineer in private practice in Discovery Bay, CA, USA. Prior to that, he was Head of Innovation for development of alternative reinforcements for concrete at BASF Construction Chemicals, now Master Builders Solutions. He is a past Chair of the TAC Technology Transfer Committee and the Technology Transfer Advisory Group of the ACI Foundation Strategic Development Council, and a past member of the ACI Board of Direction. He is a member of several ACI committees and the Concrete Research Council of the ACI Foundation. He was awarded the 1995 ACI Wason Medal for Materials Research and the 2015 ACI Henry L. Kennedy Award. He received his BSc in civil engineering from the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana, and his MS and PhD in civil engineering from the University of Kansas, Lawrence, KS, USA.