Discussion Of: "The use of the flow length concept to assess the efficiency of air entrainment with regards to frost durability: Part I - Description of the test method," by Richard Pleau and Michel Pigeon.

By: Ken Snyder

Corrigenda

On page 24, Eqn. 29 should read

$$p(S) = \frac{\partial F_s}{\partial S} = 4\pi M S^2 \, e^{-4\pi M S^3/3} \tag{1}$$

On page 25, the authors' expression in Eqn. 35 is, by definition, unity. Eqn. 35 for the cumulative density function should be

$$K'(Q) = \int_{-\infty}^{Q} k'(Q') \, dQ' \tag{2}$$

The integration variable must differ from the cumulative density function parameter.

Introduction

In an approach similar to that of Philleo (Philleo 1955), the authors have attempted to calculate the distribution of distances between random points in the paste and the nearest air void surface (paste-void proximity distribution). This approach has a distinct advantage over single parameter spacing equations (Powers 1949, Attiogbe 1993) that cannot characterize a distribution of spacings. However, like the Philleo equation, the authors' equation for the paste-void proximity distribution is an *approximation*, and is only exact for zero air content. This Discussion will demonstrate this point conclusively for monodispersed spheres. Additionally, by comparing results of a similar numerical experiment published previously to predictions based upon the authors' equation, it can be demonstrated that the authors' equation contains considerable error at a concrete air content of 5% for a zeroth-order logarithmic distribution of sphere diameters.

Sphere Centers as a Poisson Process

The approach used by the authors is based upon the assumption that the location of the sphere centers follow a Poisson process. However, they do not acknowledge this fact as such, "The probability that this point is located at a distance smaller or equal to S from the center of the nearest air void, noted $p(S)$, is given by the following equation (Philleo 1983)

$$p(S) = 4\pi M S^2 e^{-4\pi M S^3/3} \tag{3}$$

where M represents the number of voids per unit volume." In the limiting case when the air voids have zero radius the location of the centers do follow a Poisson process; however, once the air voids have a finite radius, this assumption fails because the placement of an individual sphere depends upon the placement of all the other spheres, since the spheres may not overlap.

The authors continue by using a convolution integral of the spacing between air void centers and the distribution of sphere radii (or, equivalently, the sphere diameters). Given that the probability density for the distance from a randomly chosen point in the system to the nearest sphere center follows the distribution $g(x)$, and that the sphere radii follow the probability density function $f(r)$, the probability density of being a distance s from the nearest edge of a sphere is

$$k'(s) = \int_0^\infty g(s+r)f(r)\,dr \tag{4}$$

The authors, lacking a true value for $g(x)$ used the reasonable, but incorrect, approximation given in Eqn. 3 above.

The errors induced by this approach can be demonstrated using a monodispersed sphere radii distribution. Let the monosized sphere radius distribution be represented by a Dirac delta function (Lighthill 1958):

$$f(r) = \delta(r - r_o) \tag{5}$$

Using this radius distribution, and the definition of a delta function,

$$\begin{aligned} k'(Q) &= 4\pi M \int_0^\infty (Q+r)^2 \; e^{-4\pi M(Q+r)^3/3} \; \delta(r-r_o)\,dr \\ &= 4\pi M(Q+r_o)^2\, e^{-4\pi M(Q+r_o)^3/3} \end{aligned} \tag{6}$$

This leads to the simple relation for the cumulative density function

$$\begin{aligned} K'(Q) &= \int_{-r_o}^{Q} 4\pi M(Q'+r_o)^2 e^{-4\pi M(Q'+r_o)^3/3}\,dQ' \\ &= 1 - e^{-4\pi M(Q+r_o)^3/3} \end{aligned} \tag{7}$$

For the probability density function $k'(Q)$, the authors state, "The area under the curve for $Q < 0$ thus simply corresponds to the air content of the paste fraction A_p." However, in this example for monosized spheres, the area under $k'(Q<0)$ is equal to $K'(Q=0)$:

$$K'(Q=0) \;=\; 1-e^{-\frac{4}{3}\pi M r_o^3} \tag{8}$$

which is the expected air content for *overlapping* spheres. The true air content is simply

$$A_p = \frac{4}{3}\pi M r_o^3 \tag{9}$$

However, in the limit of small air content one can use a Taylor expansion of the exponential function,

$$\begin{aligned} K'(Q=0)\big|_{A_p\to 0} \;&=\; 1-(1-\frac{4}{3}\pi M r_o^3+\cdots) \\ &\approx\; \frac{4}{3}\pi M r_o^3 \end{aligned} \tag{10}$$

and the relationship holds, to first order in A_p. Therefore, the equation derived by the authors is only exact in the limit of zero air content. For finite air contents, their equation is only an approximation. The air content in the authors' numerical experiment was 5% by total volume. In a system composed of 30% paste, as in the authors' system, the paste air content would be 16%, which is significant.

Theoretical *vs.* True Values

As a demonstration of the authors' method, they perform a numerical example using a computer to simulate the air void system and to measure circle diameters and chord lengths on a plane surface through the system. The culmination of the experiment is a table of data comparing the predicted results from circle and chord measurements to *theoretical values.*

The theoretical values shown for air content, A, specific surface, α, Powers spacing factor, $\bar{L}$, and number density of spheres, M_p, are the true values. However, as argued in the previous section, the values given for Q_{50} and Q_{98} are only *approximations.*

A previous numerical experiment (Snyder et al. 1994) used a computer that tabulated the true cumulative density function $K(Q)$. In order to use this computer program to calculate the true values for the authors' experiment, the parameters of the zeroth-order logarithmic distribution must be calculated, since the authors did not report them, from the values in the authors' Table 1 for specific surface, air content, and number density of spheres using the moments of the zeroth-order logarithmic distribution (Espenscheid et al. 1964):

$$\langle d^m \rangle = d_o^m \exp\left[(m^2 + 2m)\frac{\sigma_o^2}{2}\right] \tag{11}$$

The parameters d_o (modal diameter) and σ_o (standard deviation of the logarithms) can be calculated from the following two relations:

$$A = \frac{\pi}{6} M_p \langle d^3 \rangle = 0.05 \qquad\qquad \alpha = \frac{\pi \langle d^2 \rangle}{\frac{\pi}{6}\langle d^3 \rangle} = 200\,\mathrm{cm}^{-1} \tag{12}$$

For a system in which the unit volume is a cube one centimeter on a side, the solution of these two equations gives

$$d_o = 0.003254 \qquad\qquad \sigma_o = 0.7966 \tag{13}$$

A modal diameter of 32.54 μm is in contrast to the curve shown in the authors' Fig. 9 ("Size-distribution of the air voids used for the numerical example") which suggests a modal diameter near 100 μm. This discrepancy would cast doubt upon the results of a direct comparison between the results from the authors' numerical example to the true results calculated by computer.

Comparison to Previous Results

As mentioned above, a numerical experiment similar to the authors' has been performed previously (Snyder et al. 1994). Spheres with diameters following a zeroth-order logarithmic distribution were randomly parked in a fixed volume and both the distances from random points in the paste to the nearest air void surface (paste-void proximity distribution) and the distances between nearest neighbor spheres (void-void proximity distribution) were measured in the system. The results were compared to the predictions of Powers (Powers 1955), Philleo (Philleo 1983), and Attiogbe (Attiogbe 1993). A zeroth-order logarithmic distribution of spheres was used with the parameters $d_o = 30\mu\text{m}$, and $\sigma_o = 0.736$; the resulting distribution had a specific surface area of 300 cm^2/cm^3. An abbreviated listing of these results is summarized here in Table 1. The quantity n is the number of spheres per unit volume, $\bar{L}$ is the Powers spacing factor, F50 and F95 are Philleo factors for the 50-th and 95-th percentile of the paste-void proximity distribution, and $pv50$ and $pv95$ are the measured 50-th and 95-th percentiles of the paste-void proximity distribution of the system, representing the true values. These values are expressed along with a 95% confidence interval. Note that the air content given (expressed as a fraction) represents the air content of the air-paste system; the corresponding concrete air contents (assuming 30% paste, as the authors have) would be 0.48, 1.9, and 5.9% for three number densities reported in the table.

This model system was then analyzed using the authors' equation which estimates the spacing distribution from points exterior to the spheres. This distribution, $k(Q)$, renormalizes $k'(Q)$ to account for the volume of the system outside the spheres:

$$k(Q) = \frac{k'(Q)}{1 - A_p} \tag{14}$$

Here, two different analyses are performed. Since A_p does not equal $K'(Q = 0)$ for the authors' equation, both $1 - K'(Q = 0)$ and $1 - A_p$ were used to normalize the portion of the distribution $k'(Q)$ for $Q > 0$. The results of both analyses are given in Table 2. As expected, the authors' equation is fairly accurate for the very low air content. However, in the system with a concrete air content of about 5%, the authors' estimate is in error by a considerable percentage for both normalization factors. What is even more surprising is that, although the authors' estimate is more accurate than Philleo's for low air contents, it is less accurate at higher air contents. This is significant because the Philleo approach does not require knowledge of the distribution of sphere diameters. Rather, Philleo's equation only requires the number density of spheres, as does the authors' equation.

A qualitative comparison between the authors' estimate and the true paste proximity spacing distribution is also reported. The computer program measured the paste-void proximity cumulative density function, which was numerically differentiated and shown in Fig. 1 for the two number densities of 20000 and 240000 per cubic centimeter, corresponding to 1.6 and 19.7% air by volume of paste. As expected, the authors' approximation is a reasonably accurate estimate of the paste-void proximity distribution at low air content, but far less accurate at higher air contents.

References

Attiogbe, E.K., "Mean spacing of air voids in hardened concrete," *ACI Materials Journal* **90**, 174–181, 1993.

Espenscheid, W.F., Kerker, M., and Matijević, E., "Logarithmic distribution functions for colloid particles," *Journal of Physical Chemistry* **68**, 3093–3097, 1964.

Lighthill, M.J., *Introduction to Fourier Analysis and Generalized Functions*, Cambridge University Press, 1958.

Philleo, R.E., "A method for analyzing void distribution in air-entrained concrete," *Cement, Concrete, and Aggregates* **5**, 128–130, 1983.

Powers, T.C., "The air requirements of frost resistant concrete," *Proceedings of the Highway Research Board* **29**, 184–202, 1955.

Snyder, K.A., Clifton, J.R., "Measures of air void spacing," *Wiss. Z. Hochsch. Archit. Bauwes. (Weimar)* **40**, 155–158, 1994.

n (cm^{-3})	Air	$\bar{L}$ (cm)	F50 (cm)	F95 (cm)	$pv50$ (cm)	$pv95$ (cm)
20000	0.016	0.0450	0.0146	0.0272	0.0163±.0001	0.0291±.0003
80000	0.066	0.0247	0.0073	0.0150	0.0085±.0001	0.0161±.0002
240000	0.197	0.0136	0.0037	0.0087	0.0042±.0001	0.0089±.0001

Table 1: A partial list of results from a previous numerical experiment. The results are expressed in both number density of spheres, n, and paste air content, A. The quantities $\bar{L}$, $F50$ and $F95$ are the Powers spacing factor, and the Philleo spacing at the 50-th and 95-th percentile, respectively. The 50-th and 95-th percentile of the measured paste-void proximity distribution are labeled $pv50$ and $pv95$, respectively, along with the 95% confidence interval. (Snyder et al. 1994)

			$[1-A_p]$		$[1-K'(Q=0)]$			
n	Air	$K'(Q=0)$	K_{50}	K_{95}	K_{50}	K_{95}	$pv50$	$pv95$
(cm^{-3})			(cm)	(cm)	(cm)	(cm)	(cm)	(cm)
20000	0.016	0.012	0.0172	0.0302	0.0173	0.0304	0.0163±.0001	0.0291±.0003
80000	0.066	0.039	0.0098	0.0173	0.0100	0.0185	0.0085±.0001	0.0161±.0002
240000	0.197	0.082	0.0058	0.0099	0.0063	0.0123	0.0042±.0001	0.0089±.0001

Table 2: Comparison of the authors' predictions for the 50-th and 95-th percentiles of the paste-void proximity distribution (K_{50} and K_{95}) and the measured true values ($pv50$ and $pv95$) expressed along with the 95% confidence interval. The authors' equation for the distribution $k'(Q)$ was normalized two ways: the quantity $[1-A_p]$ (as suggested by the authors) and the quantity $[1-K'(Q=0)]$.

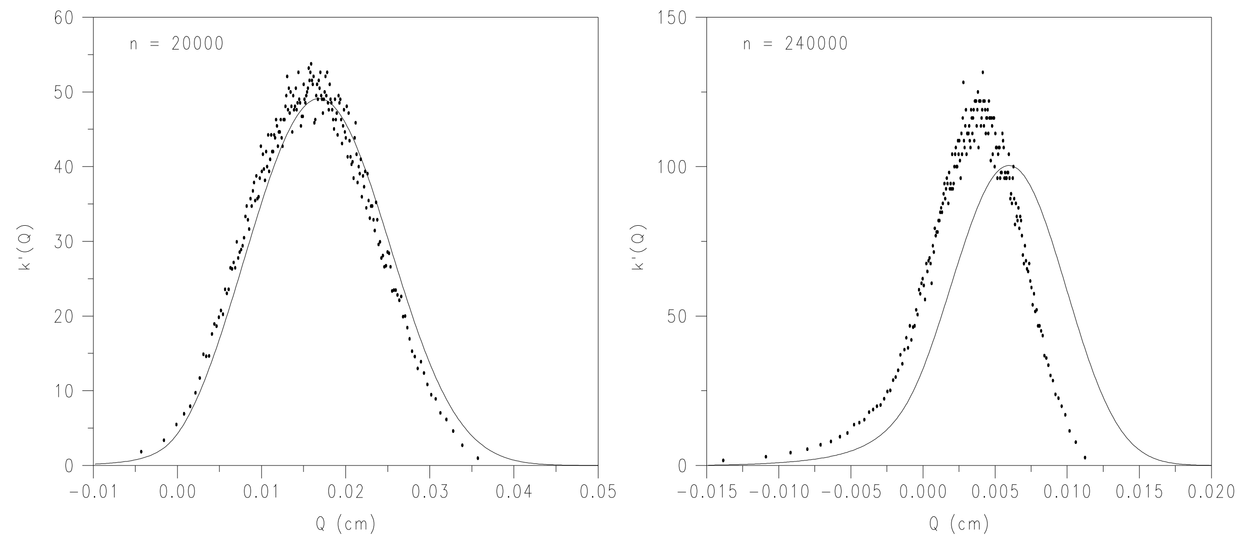

Figure 1: Comparison of the measured paste-void spacing distribution (filled circles) and the equation proposed by the authors (solid line) for two number densities of spheres, 20000 and 2400000, corresponding to paste air contents of 1.6% and 19.7%, respectively.