The Hidden Meaning of Water-Cement Ratio

Distance between cement particles is fundamental

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Concrete is always characterized by the mass ratio of water to cement (*w/c*) in the mixture. Unfortunately, for most students and many engineers, the *w/c* is an abstract number without any particular meaning. Furthermore, this number is inversely related to concrete strength: the lower *w/c*, the greater the strength.[1] People generally understand and can remember direct relationships better than inverse relationships.

In fact, *w/c* has a hidden meaning: it's directly linked to the spacing between cement particles in the cement paste. The smaller this spacing, the faster the cement hydrates fill in the gaps between cement particles, the stronger the links created by these hydrates, and most importantly, the stronger the concrete. Additionally, the smaller this spacing, the smaller the sizes of the pores created by self-desiccation and the larger the stresses generating autogenous shrinkage. Specifically, the magnitude of the capillary stress σ_{cap} created in the remaining water-filled porosity during self-desiccation or drying is given by:

$$\sigma_{cap} = \frac{2\,\gamma \cos\theta}{r} \quad (1)$$

where γ is the surface tension of the pore solution, θ is the contact angle between the pore solution and solids, and r is the radius of the meniscus in the partially water-filled pores.[2] Assuming a contact angle of 0 degrees and a surface tension of 0.072 N/m (0.0049 lb/ft), Table 1 provides values of σ_{cap} for a range of pore radii.

In this article, r will be related to the volume fraction of water that is within a given distance of any cement particle surface and examined as a function of both *w/c* and cement particle size distribution (PSD). It should be noted that it may also be possible to directly measure the internal pressures developing at early ages.[3,4] We believe the *w/c* "law" doesn't look so strange when it's considered that the ratio indirectly represents the spacing between cement particles in a cement paste. Moreover, the inverse relationship between *w/c* and strength is also easier to understand: the closer the cement particles, the stronger the concrete.

MATERIALS AND COMPUTATIONAL METHODS

Three cements were selected for analysis of their water-to-cement distance characteristics at *w/c* of 0.35 and 0.50. They included:

- Cement and Concrete Reference Laboratory (CCRL) proficiency sample cement 152 issued in January 2004 with a Blaine fineness of 410 m^2/kg;[5] and
- Two ASTM C150[6] Type I/II cements with Blaine finenesses of 310 m^2/kg and 380 m^2/kg, respectively, both from the same manufacturer but made at two different cement plants.[7]

The PSDs of these three cements, found using a laser diffraction wet method with isopropanol as the solvent, are shown in Fig. 1. These three cements provide an interesting contrast. The CCRL cement 152 has a higher

TABLE 1:
CAPILLARY STRESS VERSUS PORE RADIUS

Pore radius	Capillary stress
10 µm (0.4 mil)	0.014 MPa (2.1 psi)
5 µm (0.2 mil)	0.029 MPa (4.2 psi)
2 µm (0.08 mil)	0.072 MPa (10.4 psi)
1 µm (0.04 mil)	0.14 MPa (21 psi)
0.5 µm (0.02 mil)	0.29 MPa (42 psi)
0.2 µm (0.008 mil)	0.72 MPa (104 psi)
0.1 µm (0.004 mil)	1.4 MPa (210 psi)
0.05 µm (0.002 mil)	2.9 MPa (420 psi)

measured Blaine surface area than the Fine Type I/II cement. The CCRL 152, however, is actually the slightly coarser of the two cements, as indicated by the measured PSD curves shown in Fig. 1 where the CCRL 152 (green) curve lies to the right of the Fine Type I/II (red) curve, indicating a coarser PSD.

The water-to-cement distance function was determined using a previously developed three-dimensional hard core/soft shell (HCSS) microstructure model.[8] The model has been used to examine interfacial transition zones in concrete,[9] the use of polymeric fibers to mitigate spalling in high-performance concrete,[10] and the protected paste volume in concrete with internal curing.[11] For the current application, hard (impenetrable) spheres modeled the cement particles and soft (penetrable) shells surrounding the cement particles were used to assess the fraction of the total water volume that was within a specified distance of any cement particle surface. This assessment was performed using a three-dimensional sampling grid, with 64 million sampling points. In addition to the water fractional volume versus distance function, the program also returns a single 400 x 400 element, color-coded, two-dimensional image from the simulated three-dimensional microstructure. In the model, only water and cement are included, as no consideration is given to either entrained or entrapped air voids.

The distance function provides an indication of the radii of the menisci that will be initially formed during the processes of self-desiccation and drying, when occurring at early ages, as indicated schematically in Fig. 2. The largest pores will be those centered at locations within the water-filled capillaries that are farthest from any cement particle surfaces. These pores will be the first to empty during self-desiccation or early-age drying. As will be shown in the results to follow, this spacing is dependent on both *w/c* and the specific PSD of the cement. While simulations are employed in this paper to estimate the water-to-cement distance function, analytical solutions for spherical particles, which also require the complete cement PSD as input, are also readily available.[12] The HCSS model has been shown to provide equivalent results to the analytical solution[11] and offers the added advantage of providing a complete three-dimensional representation of the microstructure, from which two-dimensional images can be extracted.

A computational volume of 200 x 200 x 200 μm (7.9 x 7.9 x 7.9 mil) was employed for the studies presented here. Using the cement PSDs in Fig. 1 as model input, nearly 300,000 individual particles were needed to produce a *w/c* of 0.35 for the Fine Type I/II cement. In the simulations presented here, the diameters of the cement particles were limited to be in the range of 0.5 to 100 μm (0.02 to 3.9 mil). For the three PSDs in Fig. 1, microstructures were created for *w/c* values of 0.35 and 0.50, corresponding to cement volume fractions of 0.472 and 0.385, respectively, assuming a specific gravity of 3.2 for the cements.

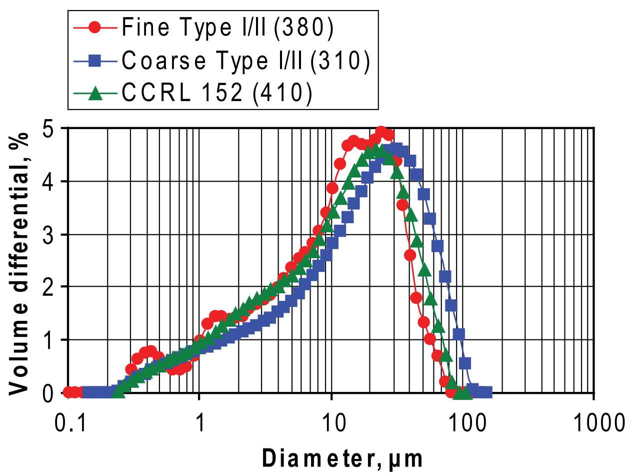


Fig. 1: Measured PSDs for the three cements examined in this study plotted as probability density functions. Blaine finenesses are indicated in parentheses (1 μm = 0.0394 mil)

RESULTS

A set of example images for the two Type I/II cements at each of the two different *w/c* is provided in Fig. 3. The brightness of the blue color representing the water provides a relative measure of the water-to-cement distance for each image. A more quantitative measure of this spacing is provided by the water-to-cement distance functions shown in Fig. 4. Clearly, both cement PSD and *w/c* influence the three-dimensional spacing distance between cement particles. The results for the three cements show that Blaine fineness is not a particularly good indication of the distance function, as exemplified by comparing the water-to-cement distance function for the 410 m^2/kg CCRL 152 cement to that for the 380 m^2/kg Fine Type I/II cement. Instead, the complete PSD is required to provide adequate input to the simulation or to the analytical solution.[12]

The size of the largest pores in the matrix, which will empty first during self-desiccation, can be found by observing

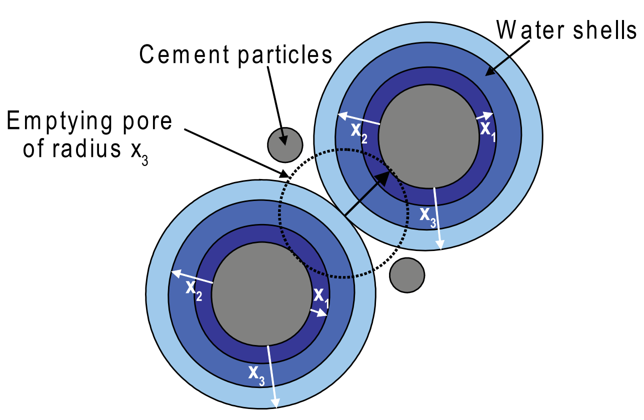


Fig. 2: Simplified schematic of relationship between water-to-cement distance function and radius of first pores emptying during self-desiccation. x_1, x_2, and x_3 represent water "shells" of increasing thickness surrounding each cement particle

the distance values corresponding to water volume fractions of 0.9 and greater. The results for the *w/c* = 0.50 cement pastes in Fig. 4 indicate that these largest pores are on the order of 1.2 to 2 μm (0.047 to 0.079 mil) in radius. These radii generate capillary stresses of about 0.1 MPa (14.5 psi). For the lower *w/c* = 0.35 pastes (Fig. 4), these initial pore sizes will range from about 0.9 to 1.6 μm (0.035 to 0.063 mil) in radius, generating about 25% higher capillary stresses. As the hydrating cement pastes continue to self-desiccate or lose additional water to drying, smaller and smaller pores will be emptied and the capillary stresses will concurrently increase, possibly exceeding the strength of the material and producing cracking if local, global, or both types of restraints are present. Once the first empty pores are produced, the initial water-to-cement distance function (Fig. 4) will no longer be valid, but the initial curves should still provide a relative indication of the progression of pore radii that will become empty during the self-desiccation or drying process because the pores are emptied from largest to smallest. Furthermore, these curves will all be shifted to smaller and smaller distances as hydration progresses and "fills in" space originally filled by water, generally from the original particle surfaces outward. In addition to containing smaller water-filled spaces between particles, a finer cement will also generally hydrate at a faster rate than a coarser one.[7] This accelerates self-desiccation processes and contributes to larger capillary stresses at equal ages.

It's interesting to note from Fig. 4 that the ratio of distances between the two Type I/II cements for any given value of water volume fraction is less than a factor of 2. From Eq. (1), an equivalent effect to coarsening the cement could potentially be achieved by using a shrinkage-reducing admixture to decrease γ, as these chemicals typically reduce surface tension by up to a factor of 2 and have been used successfully to combat autogenous shrinkage and plastic shrinkage cracking.[13,14]

In some concretes, where neither water-reducing nor high-range water-reducing admixtures are employed, the cement particles will have a tendency to flocculate. As shown by the simulation images in Fig. 5,[7] flocculation will cluster the cement particles together and thus have a tendency to increase the water-to-cement distances, leading to larger pores and lower capillary stresses. It's also shown in Fig. 5 that a cement paste prepared using a coarser cement contains larger pores, resulting in smaller autogenous stresses and strains, in agreement with experimental measurements of these quantities.[7,15] Conversely, the finer cement will hydrate more quickly, due to its higher exposed surface area, and exhibit higher strengths, due to both the smaller pores and its increased hydration rate.[7] A further complication in concretes and mortars versus pastes will be the likely presence of interfacial transition zones (ITZs)[9] or other sources of microstructural inhomogeneities[16] that will also result in larger local water-to-cement distances. For ITZs, the extent of the ITZ region is approximately equivalent to the median cement particle diameter.[9]

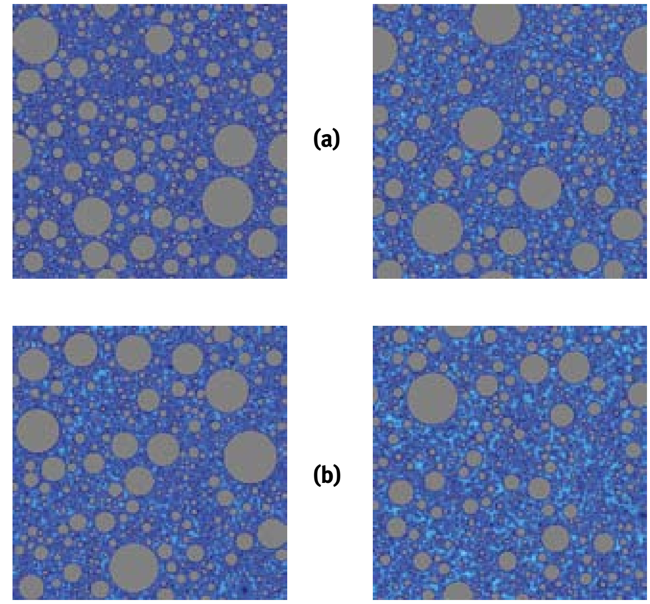


Fig. 3: Two-dimensional images [200 x 200 μm (7.9 x 7.9 mil)] of (a) Fine Type I/II cement; and (b) Coarse Type I/II cement with *w/c* = 0.35 (left) and *w/c* = 0.50 (right). Cement particles are gray and shades of blue indicate distances of water from nearest cement particle surface, with lighter blues indicating a greater distance

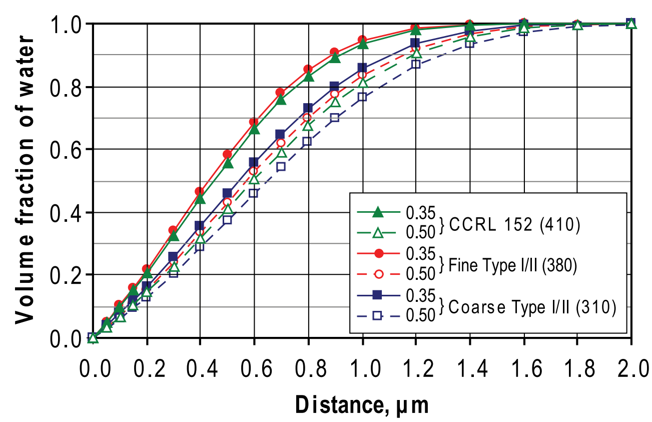
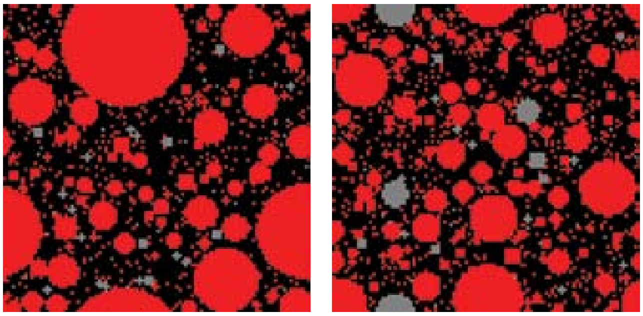


Fig. 4: Water-to-cement distance function for the three cements at *w/c* of 0.35 and 0.50 (1 μm = 0.0394 mil)

NEEDS AND PROSPECTUS

As illustrated by the three cements examined in this study, a complete PSD is critical to accurately determining a water-to-cement distance function. Unfortunately, no standard test method for measuring PSD of cement currently exists. ASTM International C01.25 Subcommittee on Fineness, however, is working on developing standard measurement techniques for PSD.

A Web site has been established for performing these simulations and returning results to the user at **http://ciks.cbt.nist.gov/cementspacing.html**. Both a two-dimensional



(a) (b)

Fig. 5: Two-dimensional slice images [100 x 100 μm (3.9 x 3.9 mil)] from simulated flocculated microstructures for *w/c* = 0.35 cement pastes: (a) Coarse Type I/II cement; and (b) Fine Type I/II cement. Model cement particles are red and model gypsum particles are gray[7]

image, such as those shown in Fig. 3, and a table of the water-to-cement distance function are available as outputs. It's hoped that the availability of such a computational tool for determining the water-to-cement distance function will remove some of the hidden meaning of *w/c* and provide a concrete demonstration of the linkages between *w/c*, cement PSD, and particle spacing.

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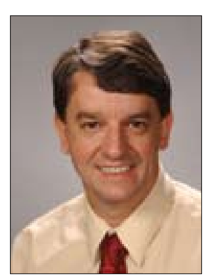

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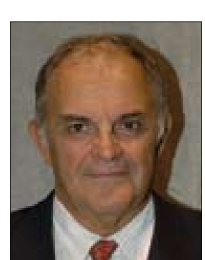

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