EFFECTS OF CEMENT PSD ON POROSITY PERCOLATION AND SELF-DESICCATION

Cement PSD and self-desiccation

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Abstract

The degree of self-desiccation in field concrete depends on the availability of external water to replace that consumed due to the chemical shrinkage that occurs during cement hydration. As the cement hydrates, the capillary porosity depercolates, drastically slowing down this rate of external water ingress. In this paper, computer simulations are used to investigate the effects of cement particle size distribution (PSD) on capillary porosity percolation and the empty porosity created by chemical shrinkage. In addition, simulations are conducted with a single aggregate in the model microstructure to investigate the effects of cement PSD on interfacial transition zone (ITZ) microstructure at this aggregate interface. Because the largest pores empty first during self-desiccation, the ITZ region in systems containing aggregates is characterized by the presence of a large volume fraction of empty porosity relative to that found in the bulk paste. The cement PSD influences both the volume and size distribution of empty pores, which will in turn control the internal relative humidity reduction and autogeneous shrinkage for these materials. Thus, cement PSD is one material parameter available for engineering the self-desiccation and autogeneous shrinkage behavior of low water-to-cement ratio concretes.

Keywords: Chemical shrinkage, hydration, interfacial transition zone, microstructure, particle size distribution, percolation, self-desiccation, simulation.

1 Introduction

In 1935, Powers [1] reported that during cement hydration, external water is absorbed by the hydrating cement paste to replace that consumed by chemical shrinkage (the hydration products occupying a smaller volume than the reactants). When external water is not present or not readily available to the hydrating system, self-desiccation occurs and empty pores are created within the microstructure. Based on the Kelvin-Laplace equation, these empty pores will cause a reduction in the internal relative humidity (*RH*) [2], in turn inducing capillary stresses within the remaining capillary water. These stresses will cause a measurable deformation, referred to as the autogeneous shrinkage of the mortar or concrete specimen.

Self-Disiccation and Its Importance in Concrete Technology, 2nd (Second) International Research Seminar. Proceedings. June 18, 1999, Lund, Sweden, Persson, B.; Fagerlund, G., Editors, 127-134 pp, 1999.

The magnitude of autogeneous shrinkage in conventional concrete mixtures is very small, but increases dramatically as the water-to-cement (w/c) ratio decreases to the values used in high-performance concretes.

The reduction in internal *RH* is mainly dependent on two factors: the volume of empty pore space created and the pore size distribution of the cement paste [3]. Similar to a mercury intrusion experiment where the largest connected pores first fill with mercury, during self-desiccation, the largest pores will empty first. Thus, the moisture content vs. relative humidity tends to follow the measured desorption isotherm of the material [4]. When attempting to engineer the autogeneous shrinkage and internal *RH* of a concrete for field use, one can attempt to regulate either the amount of empty pore space, its size distribution, or both.

One material parameter that influences both of these properties is the particle size distribution (PSD) of the cement. Naturally, the size distribution of the cement particles has a large influence on the initial and hydrated pore size distribution of the cement paste. While the volume of chemical shrinkage is proportional to hydration [1] and would be expected to be independent of cement PSD at equal degrees of hydration, the availability of external water does depend on the cement PSD in the following manner. In measuring the chemical shrinkage of a variety of cement pastes, Geiker [5] has shown that for a given w/c ratio, there exists a critical degree of hydration beyond which the rate of water ingress is unable to keep up with that needed to maintain saturation. This point corresponds to the depercolation of the capillary pore space [6, 7]. Once the capillary porosity becomes disconnected, water must penetrate via the much smaller pores in the *C–S–H* gel, so that the penetration rate slows by one order of magnitude or more. Recently, simulation studies have indicated that this depercolation of the capillary porosity is dependent on the cement PSD [8], with coarser cements requiring a larger degree of hydration to achieve depercolation. Thus, under proper curing conditions, a coarser cement may result in a reduction in both the empty porosity created by chemical shrinkage and the autogeneous shrinkage of the specimen. In this paper, computer simulations are applied to studying the influence of cement PSD on capillary porosity percolation, empty porosity created by chemical shrinkage, and interfacial transition zone (ITZ) microstructure.

2 Computer Modelling Techniques

All simulations presented in the results section were conducted using the NIST 3-D cement hydration and microstructural development model, which has been described previously [9]. The PSDs used were measured on actual cements [8] and bracket the PSDs currently produced by cement manufacturers. The fine cement had a median particle diameter of about 5 μm and a Blaine surface area of 640 m^2/kg, while the coarse cement had a median particle diameter of about 30 μm and a Blaine surface area of 210 m^2/kg. The composition of the cement determined by quantitative microscopy was 59 % C_3S, 25.9 % C_2S, 0.6 % C_3A, and 14.2 % C_4AF, with hemihydrate added at a mass percentage of 4.6 % [8]. Recently, a number of properties of these two model cements have been studied in detail [10]. Both cement paste and concrete (w/c=0.3) microstructures were simulated. In the latter case, the presence of an aggregate is simulated by placing a 2-pixel wide sheet of aggregate through the middle of the 3-D microstructure. For the 30 μm cement, simulations were also conducted with a 10 % silica fume replacement of cement (mass basis). The silica fume, modelled as 0.5 μm particles, reacts with the calcium hydroxide produced during hydration and also results in a reduction in the overall Ca/Si ratio of the *C–S–H* gel [11, 12]. The cements were modelled as either 100 × 100 × 100 (1 μm/pixel) or 200 × 200 × 200 (0.5 μm/pixel) 3-D microstructures.

The hydration simulations were executed under two different curing conditions. In one case, the hydration was executed under totally sealed conditions, so that no additional water was available to replace that consumed due to chemical shrinkage. In this case, empty porosity is created within the microstructure to account for the water "volume" lost due to chemical shrinkage [9]. In the second case, referred to as saturated/sealed curing, the hydration was executed under saturated conditions until the capillary porosity became depercolated, at which point all subsequent hydration was performed under sealed conditions. Under saturated conditions, no empty porosity is created within the microstructure during hydration, as it is assumed that all needed water is readily available from the external environment to replace that "lost" via chemical shrinkage. Previously, Powers has suggested the moist curing of field concrete only to the point where the capillary porosity depercolates [13], as subsequent curing beyond this may be of little value.

3 Results

3.1 Percolation and chemical shrinkage in cement pastes

At equivalent w/c ratios, the initial average interparticle spacing will be greater for a coarser cement system as can be seen in Fig. 2, subsequently presented in section 3.2. This will result in a greater degree of hydration being required to disconnect the capillary pore network. A quantitative comparison of depercolation of capillary porosity for the systems examined in this study is provided in Fig. 1. While the 5 μm system depercolates at a capillary porosity of about 0.21, the 30 μm system capillary pore network remains percolated down to a porosity of about 0.15. The addition of 10 % (replacement for cement on a mass basis) silica fume particles, much finer than the 30 μm cement, slightly shifts the percolation threshold to a higher porosity of about 0.16. Since water is easily imbibed into the cement paste before depercolation of the capillary porosity, the coarser cements would be expected to provide an enhanced "curability", as they will continue to imbibe water after the finer cements' pore networks have depercolated [8].

This shift in porosity percolation threshold will also influence the empty porosity created by chemical shrinkage and the resultant autogeneous shrinkage occurring in water-cured cement pastes. Table 1 summarizes the empty and water-filled porosity present after executing 5000 cycles (about 25,000 hours or 1040 days) of the hydration model for both saturated/sealed and sealed curing conditions. The empty porosity due to chemical shrinkage for the finer cement is greater than that for the coarser cement for two reasons. First, the increased hydration of the finer cement results in an increase in chemical shrinkage, particularly evident in the systems hydrated under sealed conditions. Second, because the finer cement switches from saturated to sealed curing (when the capillary porosity depercolates) at a higher capillary porosity, it produces a greater amount of empty porosity during the "sealed" hydration stage. At a degree of hydration of 0.59, equivalent to that ultimately achieved by the 30 μm cement, the empty porosity volume fraction of the 5 μm cement is 0.024, 60 % higher than that observed for the coarser cement.

In Table 1, the presence of 10 % silica fume is seen to result in a slight increase in the volume of empty porosity for both curing conditions, in agreement with previous simulation results [14]. While not directly addressed by the simulations, the cement PSD and inclusion of silica fume will also affect the pore size distribution of the hydrated cement paste. In two systems with equivalent total porosities and equivalent amounts of chemical shrinkage, the

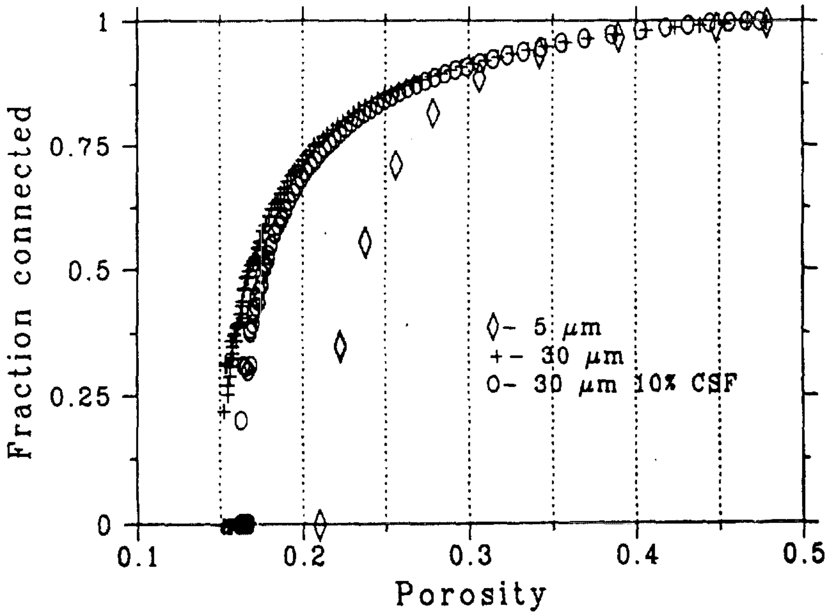

Fig. 1: Fraction connected porosity vs. total porosity for w/c=0.3 cement pastes of varying cement PSD and silica fume content. System size is 200 × 200 × 200 (0.5 μm/pixel).

system with finer pores will exhibit a greater reduction in internal *RH* and a greater amount of autogeneous shrinkage [15]. In general, a reduction in empty porosity (due to chemical shrinkage) and resultant autogeneous deformation should be observed when using a more coarsely ground cement [10].

3.2 Interfacial transition zone (ITZ) microstructure

In addition to affecting the overall percolation of the capillary porosity and the amount of empty porosity, the cement PSD also has a significant effect on the local microstructure of the ITZ. It has been previously illustrated using computer modelling that the thickness of the ITZ region will be on the order of the median diameter of the cement PSD [16]. Thus, the use of a coarser cement will increase the thickness of the ITZ region and also result in the presence of larger "pores" in this region. Since the largest pores empty first during self-desiccation, a large fraction of empty porosity may be created within the ITZ region

Table 1. Porosity of cement pastes after 5000 cycles of hydration (w/c=0.3)

PSD	Silica fume (%)	Empty porosity fraction	Water-filled porosity fraction	Degree of hydration
5	0	0.031	0.012	0.71
5^a	0	0.077	0.009	0.64
30	0	0.015	0.083	0.59
30^a	0	0.070	0.043	0.57
30	10	0.021	0.066	0.57
30^a	10	0.074	0.048	0.52

^{a}totally sealed hydration

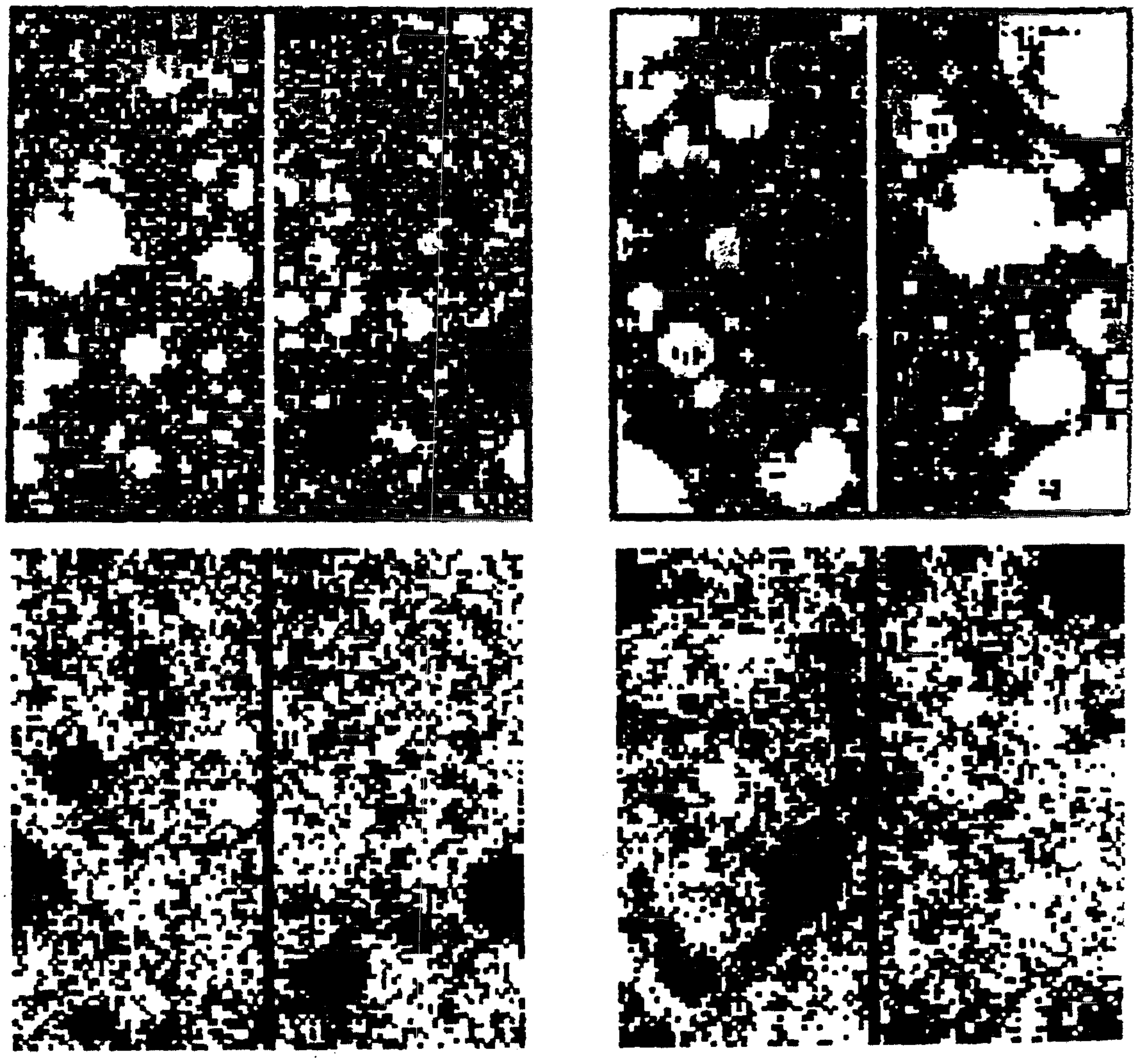

Fig. 2: Original and final 100 × 100 2-D microstructure images for upper left: original w/c=0.3 PSD=5 μm, upper right: original w/c=0.3 PSD=30 μm, lower left: final w/c=0.3 PSD=5 μm, and lower right: final w/c=0.5 PSD=30 μm. Final images are for hydration under totally sealed conditions. In the original images, phases from brightest to darkest are: C_3S, C_2S, C_3A, C_4AF, hemihydrate, and porosity. In the final images, phases from brightest to darkest are: $C-S-H$ gel, other hydration products, unhydrated cement, and empty porosity. Central bar extending across the microstructure is the flat plate aggregate.

[10]. This is illustrated in Fig. 2 which shows 2-D plane sections from the initial and final microstructures (from the 3-D model) for the two different cement PSDs. One can clearly observe the larger pore sizes present with the coarser cement, particularly in the ITZ region. The final images show that often these larger pores empty during hydration, creating an ITZ microstructure that is significantly different from that of the bulk cement paste. While these large pores are likely detrimental from a strength viewpoint, they may actually reduce the autogeneous shrinkage in these systems, as for the same amount of chemical shrinkage, the emptying of larger pores will result in less of a decrease in internal *RH* and thus, less measurable autogeneous shrinkage [15].

A quantitative analysis of this phenomena is provided in Fig. 3, which provides plots of the water-filled and empty capillary porosity as a function of distance from the aggregate surface for the initial and final microstructures. The appearance of a local maxima at a distance of about 5 pixels in the final empty porosity curves, particularly prominent for the systems cured under totally sealed conditions, corresponds to the large empty pores observed in the final microstructural images provided in Fig. 2. The peak is seen to be much higher for the coarser cement, due to the inefficient packing of the cement particles in the vicinity of the aggregate surface and the larger average pore size. For the water-filled porosity, the profile increases basically in a monotonic fashion as the aggregate is approached, due both to the initial cement particle packing and the one-sided growth effect [17]. For the empty porosity, however, the value actually decreases very near to the aggregate surface, as the pores a finite distance from the aggregate are first emptied during self-desiccation and a "thin (several pixel) water film" remains on the aggregate surface to be filled in by subsequent hydration.

4 Conclusions

The effects of cement particle size distribution on self-desiccation in cement pastes have been examined using computer simulations. Coarser cements influence self-desiccation in these systems by:

1. increasing the hydration needed to depercolate the capillary pore network,
2. increasing the average pore size due to particle spacing considerations, and
3. modifying the interfacial transition zone microstructure by introducing more and larger pores which may remain as empty pores following hydration.

All of these effects should result in a reduction in the measured autogeneous shrinkage of cement pastes and concretes produced using a coarser cement, in agreement with the experimental results of Jensen [18].

5 References

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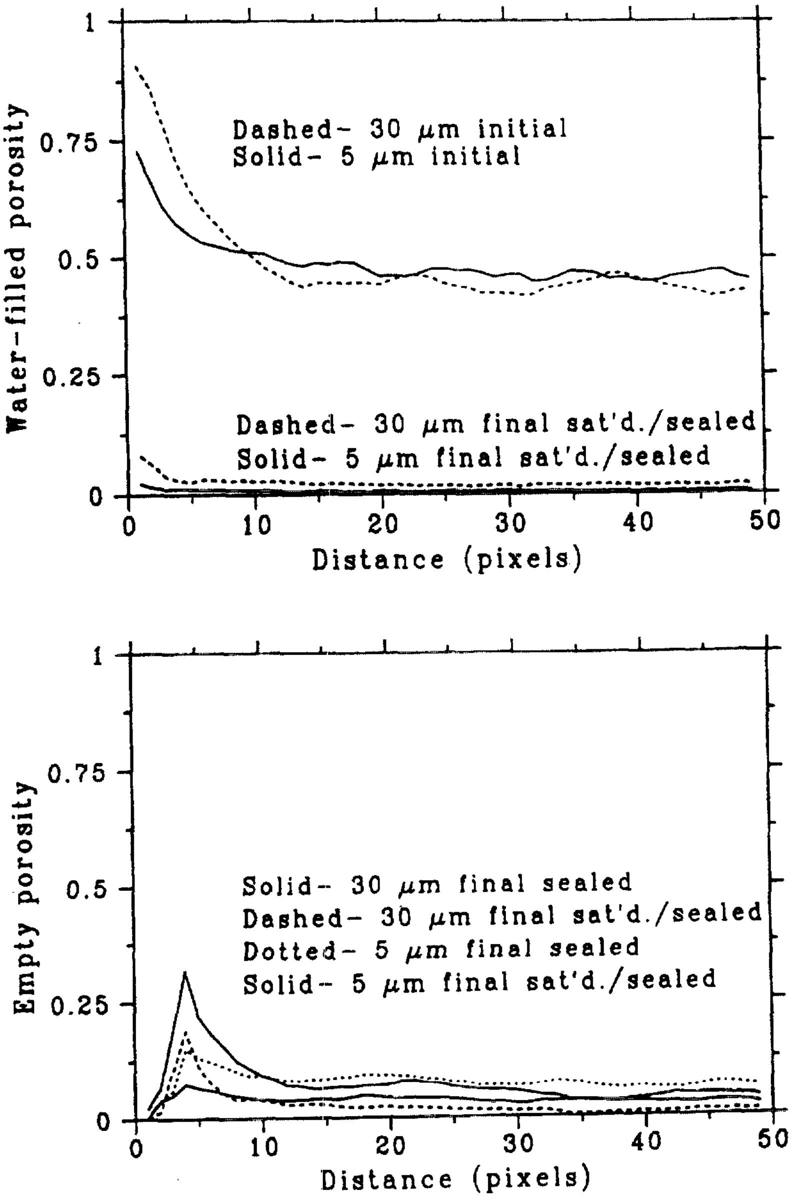

Fig. 3: Water-filled (upper) and empty (lower) porosity volume fractions vs. distance from aggregate, w/c=0.3. Final curves for empty porosity are for hydration under sealed or saturated/sealed curing conditions.

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