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Communication

# An argument for using coarse cements in high-performance concretes

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## Abstract

The NIST cement hydration microstructural model and experimental studies are used to investigate the effects of particle size distribution and water-to-cement ratio on hydration kinetics. Cement hydration is limited by the availability of water at the cement particle surfaces. Because a reaction layer forms around each cement particle during hydration, this availability is controlled by two factors: the overall water-to-cement ratio and the particle size distribution of the cement. As the water-to-cement ratio is decreased, the effects of particle size distribution on ultimate degree of hydration become less significant. Thus, in the new generation, high-performance concretes, more coarsely ground cements may provide good performance, resulting in substantial energy savings due to a reduction in grinding time. This implies that cement fineness should be optimized based on the mixture proportions of the concrete in which it will be used. Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* High-performance concrete; Hydration; Microstructure; Modeling; Particle size distribution

The importance of particle size distribution (PSD) in influencing cement hydration kinetics and strength development is well recognized [1–6]. For a fixed cement content, a reduction in median particle size generally results in increased hydration and a higher compressive strength. Thus, Portland cement finenesses have increased over the years to produce concretes with improved properties, such as higher early strengths. Of course, adequate detail must be given to the additional effects of increasing cement fineness, such as an increased water demand and a more rapid heat generation in the concrete structure.

In recent years, further improvements in concrete properties have been produced in so-called high-performance concretes. In these systems, a substantial reduction in water-to-cement (w/c) ratio is achieved through the use of superplasticizers, with further improvement of some properties obtained through the addition of pozzolanic material such as silica fume and fly ash. One consequence of the lower w/c ratio is that not all of the cement in the concrete mixture participates in the hydration reactions. It is generally accepted that for w/c ratios less than approximately 0.42, unhydrated cement must remain, as all of the available space is filled in with hydration products [6]. Unreacted cement will be present regardless of the PSD of the cement. This raises an important question: Do coarser cements offer sufficient performance for some high-performance concretes? In this communication, the NIST computer model for cement hydration and microstructure development will be applied to a preliminary exploration of this issue.

## 1. Experimental and modelling approach

The NIST microstructural model has been described in detail elsewhere [7,8]. Using cellular automaton rules, it operates on a three-dimensional digitized microstructure consisting of a volume of pixel elements to simulate the reactions between cement and water. For the present study, two modifications were made to the model. The reaction of hemihydrate to produce gypsum was included so that various forms of sulfate could be studied. Further, the dissolution algorithm was changed so that the 12 next nearest neighbor pixels (in three dimensions), in addition to the six immediate neighbors, are considered as possible dissolution sites. This latter modification increases the long-term hydration of the larger ($>10$ $\mu$m) cement particles in the model cements.

The model was applied to simulate the experimentally observed hydration behavior of seven cements of various finenesses made from the same clinker. Laser diffraction techniques were used to determine the PSD of each of the cements, and quantitative X-ray diffraction was applied to determine the fraction of tricalcium silicate ($C_3S$) that had

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reacted at ages of 1, 2, 3, 4, 7, 14, 28, and 56 days. The cumulative PSDs are shown in Fig. 1. The cement PSDs will be referred to as 5, 10, 15, 20, 25, 30, and 40 μm, proceeding from left to right in Fig. 1, corresponding approximately to the average size obtained in fitting the PSDs to a Rosin-Rammler distribution [6]. The curves designated as 10 and 15 μm would be typical of ordinary Portland cements [9]. The composition of the cement, determined by quantitative microscopy, is 59% tricalcium silicate, 25.9% dicalcium silicate, 0.6% tricalcium aluminate, and 14.2% tetracalcium aluminoferrite, with hemihydrate added at a mass percentage of 4.6%.

The measured PSDs and clinker compositions were used in constructing model initial microstructures for cement pastes with w/c ratios of 0.246, 0.3, and 0.5. The calculations for the w/c = 0.5 model runs were used as a baseline, because experimental measurements were also performed at this w/c ratio. These initial systems were hydrated using the NIST microstructural model to study the effects of PSD on hydration kinetics, percolation of porosity, and consumption of water. For the two lower w/c ratio cement pastes, the hydration simulation was executed under saturated conditions until the capillary porosity depercolated, at which point all subsequent hydration was executed under sealed (no water ingress) curing conditions [10].

## 2. Results and discussion

To calibrate the model to real time, one parameter that relates model cycles to time as given in Eq. (1):

$$\text{Time (h)} = B * \text{cycles}^2 \tag{1}$$

needs to be specified [7]. Based on the experimental measurements for w/c = 0.5 at 20°C, B was set at a value of 0.001 (compared with previously used values of 0.0017 [7] and 0.0011 [11], both at 25°C). Using this factor, Fig. 2 provides a plot of the conversion of tricalcium silicate as a function of time for both the model and real systems. The agreement between model predictions and experimental observations in general is excellent, falling well within the relative standard uncertainty of 13% for the experimental measurements. This suggests that the model adequately describes the effects of PSD on hydration kinetics. It is clear from Fig. 2 that finer grinding results in enhanced hydration at all ages investigated in this study.

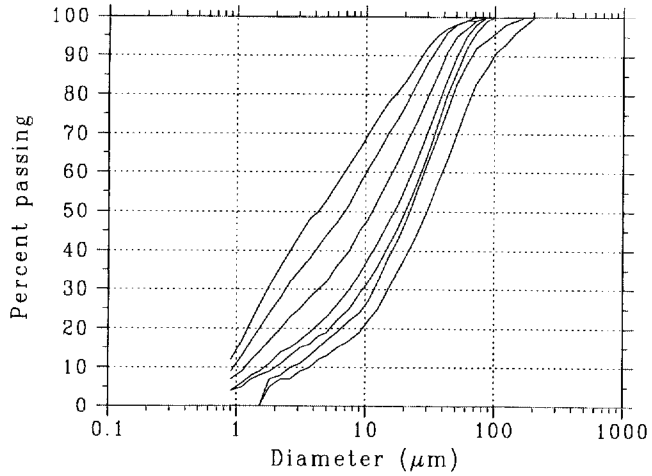

Fig. 1. Measured particle size distributions for the seven Portland cements.

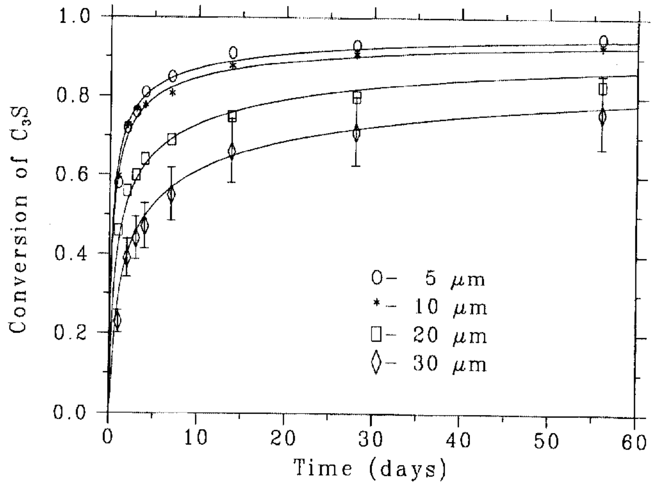

Fig. 2. Experimental (data points) and model (lines) results for degree of hydration of $C_3S$ for w/c = 0.5 at 20°C. Error bars for 30-μm data points indicate relative standard uncertainty in experimental measurements.

The results in Fig. 2 are for a w/c ratio of 0.5, a typical value for ordinary concrete, but much too high for a high-performance concrete. With this in mind, simulations were conducted at two much lower w/c ratios that are more typical of high-performance concretes (0.246 and 0.3). Fig. 3 provides plots of degree of hydration (based on the total cement reacted) vs. time for the 5-, 20-, and 30-μm PSDs for the three different w/c ratios. As was the case for the conversion of the tricalcium silicate, at a w/c of 0.5, substantial differences in the overall hydration kinetics are observed. However, the later age differences are much less significant for w/c = 0.3 pastes and are practically nonexistent for w/c = 0.246 pastes. The ultimate degrees of hydration of these pastes are limited by initial water content and not by the PSD of the cement, within the range investigated in this computer study. Thus, the benefits of additional grinding in enhancing long-term hydration may be minimal for these low w/c ratio systems.

A possible additional benefit of using a more coarsely ground cement in a high-performance low w/c ratio concrete may be found in terms of its "curability." In high-performance concretes, due to the low w/c ratio, the capillary porosity depercolates relatively early in the hydration process [12], making it difficult to provide extra water to replace that consumed by chemical shrinkage [10]. But, results of simulations shown in Fig. 4 suggest that this depercolation may actually occur at a lower capillary porosity (e.g., more hydration) for the more coarsely ground ce-

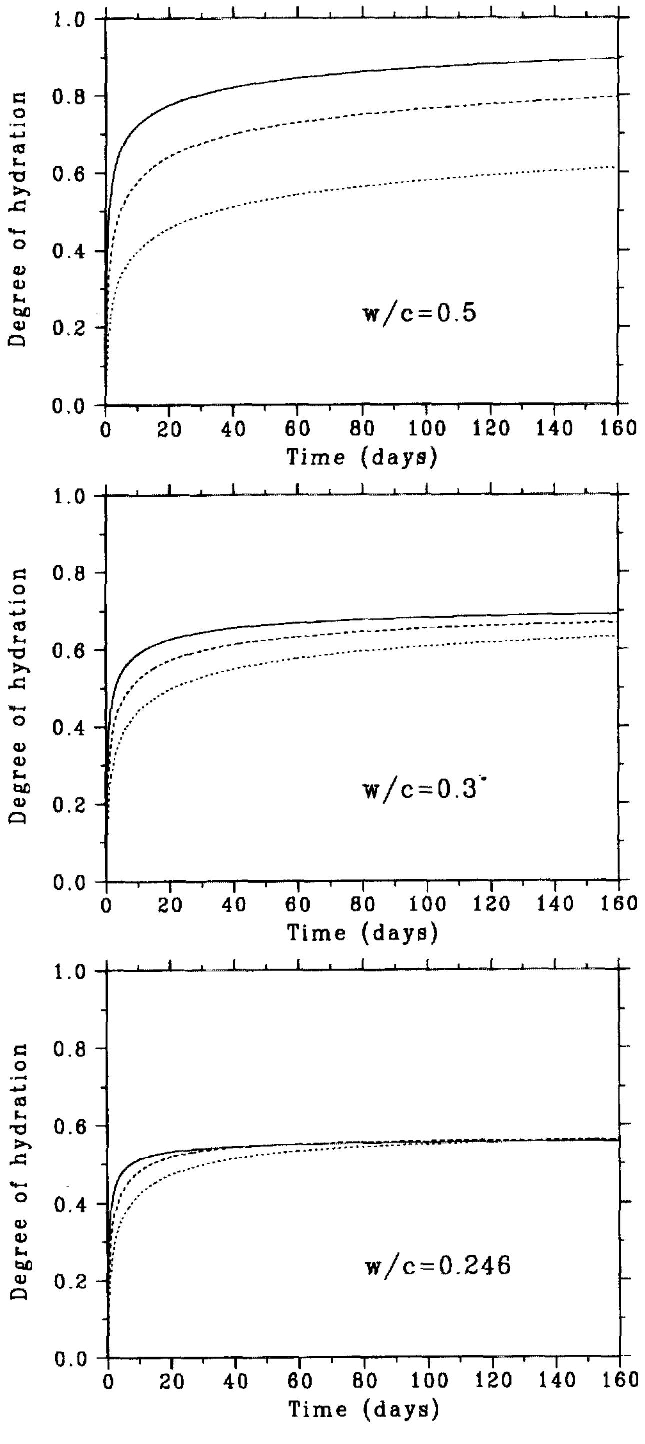

Fig. 3. Model results for degree of hydration of the cement for w/c = 0.5, 0.3, and 0.246. In all three plots, the solid line is for 5 μm cement, the dashed line is for 20 μm, and the dotted line is for 30 μm.

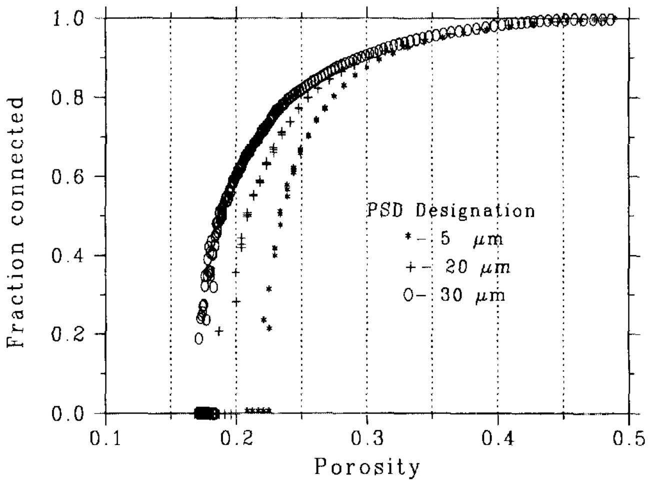

Fig. 4. Model results for capillary porosity percolation for w/c = 0.3 cement pastes.

ments. This implies that, in the field, these concretes may imbibe water for a longer period of time, which would provide a saturated system for better curing. This should result in both an increase in the long-term degree of hydration and a reduction in autogenous shrinkage, assuming, of course, that adequate attention is paid to curing procedures in the field. If poor curing practices are followed, the finer cements may perform better because their capillary porosity will depercolate and "seal in" the remaining water at an earlier hydration time. For the w/c = 0.3 pastes, the depercolation occurs at about 22%, 20%, and 17% porosity for the 5, 20, and 30-μm cements, respectively. These porosities correspond to curing times of approximately 1, 3, and 13 days at 20°C. For w/c = 0.246 pastes, the corresponding curing times are 9 hours, 1 day, and 5 days.

Whereas this study is preliminary in nature, it points out that optimizing the cement for a high-performance concrete may be different than for a conventional one. In high-performance concretes, a superplasticizer and very small (<1 μm) silica fume particles often are added. With a coarser cement, less superplasticizer should be required to achieve an adequate dispersion of the cement particles. The small silica fume particles improve interfacial transition zone (ITZ) packing and may affect the percolation characteristics of the capillary pore network. One can envision that the packing in such a (silica fume-coarse cement) system might be equivalent to that in a gap-graded aggregate concrete. The silica fume also will enhance the early strength development, offsetting the expected decrease in this property due to the more coarsely ground cement. Recently, microfine cements have been introduced that provide many of the same benefits as silica fume in improving ITZ microstructure and strength [9]. Concretes using these cements will be explored in more detail in future research.

## 3. Conclusions

It has been shown that the effects of w/c ratio and cement PSD must be considered concurrently when studying hydration kinetics of Portland cements. For low w/c ratios, at long enough times, model results indicate that the effects of PSD on degree of hydration become insignificant. This implies that for high-performance concretes, coarser cements may suffice, which could result in energy savings in cement manufacturing. An additional potential benefit of the coarser cements, assuming proper curing practices are followed, may be enhanced "curability," as their capillary porosity will remain percolated to allow water imbibition for longer curing times. This study points out that when optimizing a cement for concrete performance, one must first consider the concrete mixture proportions in which it will be employed. Finally, it has been demonstrated that the NIST microstructural model provides a convenient framework for studying the optimization of concrete systems.

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