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HYDRATION OF PORTLAND CEMENT: THE EFFECTS OF CURING CONDITIONS

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ABSTRACT In this paper, experimental and computer modelling studies of the effects of curing on hydration are presented. Degree of hydration has been quantified for saturated, sealed, and 90% relative humidity ambient environments, all at 25 °C. For both the saturated and the sealed curing conditions, experimental results for degree of hydration and scanning electron microscopy images are compared to those generated using the NIST cement paste microstructural model. Implications for the field curing of concrete are also addressed.

INTRODUCTION

Proper curing of concrete is paramount for obtaining optimum performance from a given set of mixture proportions. For high-performance concretes, curing becomes even more important, due to the typically lower water-to-cement (w/c) ratios and the increased propensity for early age cracking due to thermal and self-desiccation stresses (Henrichsen and Laugesen, 1995). Besides the water which is removed due to exposure to an ambient environment, additional empty capillary porosity is created within the cement paste component of the concrete due to the chemical shrinkage that accompanies the cement hydration reactions, quantified many years ago by Powers (Powers, 1935), but also the subject of much recent research (Geiker, 1983, Hua *et al.*, 1995, Tazawa *et al.*, 1995, and Justnes *et al.*, 1996).

The creation of empty capillary pore space has two major effects on the evolving cement paste system. First, the resultant capillary pressures induce shrinkage stresses within the cement paste microstructure, causing a measurable external physical shrinkage (Hua *et al.*, 1995 and Justnes *et al.*, 1996). The magnitude of these stresses (at relative humidities where some of the capillary pore space is still filled with water) will be influenced by the relative humidity (RH), in the following manner. The Kelvin-Laplace equation can be used to relate the relative humidity to the capillary condensation process:

$$\ln(\frac{\mathbf{RH}}{\mathbf{100}}) = -\frac{K\gamma V_m}{RT} \tag{1}$$

where γ is surface tension, V_m is the molar volume of water, R is the universal gas constant (8.314 J/(mol· K)), T is absolute temperature, and K is the average curvature of the surface of the condensed water (equivalent to $2/r$ for a spherical droplet where r is the radius of the droplet/pore). Thus, at a given RH, water will condense in all pores of curvature greater than or equal to K (pore radius less than or equal to r). The induced capillary pressure, $\sigma_{\text{capillary}}$, is then given:

$$\sigma_{\text{capillary}} = K\gamma = -\frac{\ln(\frac{\mathbf{RH}}{\mathbf{100}})RT}{V_m}. \tag{2}$$

According to Eq 2, the induced capillary pressure is directly proportional to ln(**RH**). The measured shrinkage should be a function of this capillary pressure and the moisture content (saturation) of the concrete (Mackenzie, 1950 and Bentz *et al.*, 1996). Indeed, field

measurements have shown that both moisture content and measured concrete shrinkage are proportional to variations in ambient RH (Granger *et al.*, 1994). In the case of hydration under sealed conditions, the autogenous shrinkage stresses will be influenced by the internal RH reduction due to the chemical shrinkage. As first quantified in 1940 (Gause and Tucker, 1940), this RH reduction can be quite substantial, with RH values as low as 70% measured for low w/c (< 0.3) ratio cement paste and concrete systems (Mjornell, 1994 and Persson, 1996). According to Eq 2, the induced capillary pressures will be seven times greater in a system with an RH of 70% vs. one with an RH of 95%, which may be one reason why high-performance concretes are often more susceptible to early age cracking.

The second effect of the creation of empty capillary pores will be a change in the hydration kinetics for the cement paste (Powers, 1947 and Molina, 1992). Because cement hydration reactions generally proceed by a dissolution/precipitation mechanism, the empty pore space created due to drying or self-desiccation is no longer available to be filled with hydration products, so that the hydration will slow down and effectively terminate at a lower degree of hydration than that which could be achieved under saturated conditions. The remainder of this paper will focus on this latter effect, using a combination of experimental and computer modelling techniques to quantify the effects of curing conditions on the measured degree of hydration of a series of cement pastes.

EXPERIMENTAL PROCEDURES

Saturated and Sealed Specimens

Details for the two ASTM Type I portland cements used in this study, Cements 115 and 116 issued by the Cement and Concrete Reference Laboratory, can be found elsewhere (Bentz, 1996). In all cases, the cement and the necessary mixing water, w/c=0.3 or 0.4, were conditioned at 25 °C overnight and then mixed together by hand in a sealed plastic bag for two to three minutes. For hydration under saturated and sealed conditions, samples on the order of ten grams were stored in capped plastic vials at 25 °C until measuring the non-evaporable water content, typically after ages of 1, 3, 7, 14, 28, 56, and 90 days. For the saturated samples, approximately 1 mL of water was added on top of the cement paste to maintain saturation. Non-evaporable water was quantified as the weight loss between 105 °C and 950 °C, corrected for the loss on ignition for the dry cement powder. These values were converted to degrees of hydration based on measurements performed on fully hydrated specimens (w/c=3.0, continuously ground in a jar mill for 28 days), which yielded values of 0.226 and 0.235 g H_2O/g cement for Cements 115 and 116, respectively. For Cement 115, two samples, one saturated and one sealed hydration, were removed after 94 days curing and prepared for viewing in the scanning electron microscope (SEM).

Curing Under 90% RH

The companion controlled relative humidity experiments were performed using Cement 116. The paste samples were mixed in a sealed plastic bag for 5 minutes. The specimen holders consisted of two 1.6 mm-thick sheets of hydrophobic polytetrafluoroethylene (PTFE) cut to 127 mm ×152 mm. One of the sheets had been punched with twenty three 25 mm-diameter holes, and the two sheets were adhered together using a silicone sealant. The mixed cement paste was spread over the 25 mm holes, filling them to form discs of uniform thickness. The fresh specimens were then placed in a 25°C, 100% RH environment.

To assess the combined effects of RH and time on the hydration of cement paste, the

specimens were stored at 100% RH for 6 and 12 hours, and 3 and 7 days before being placed into an environment of 25°C and 90% RH. Here, the specimens were maintained in an atmosphere free of CO_2, to avoid carbonation effects, achieved by using an overpressure of pure nitrogen. Prior to entering the 90% RH environment, the two sheets were pried apart, exposing both sides of the hardened specimens (the sheets for the 0.3 w/c pastes were pried apart after 24 hours, or sooner as required). Periodically, the degree of hydration was determined by measurement of the non-evaporable water content, as described above, from a sample consisting of two paste discs.

Computer Simulations

In addition to the experimental studies, computer simulations were performed using the NIST cement paste microstructural model (Bentz, 1996). For each of the two cements, initial 3-D cement particle images were created for w/c=0.3 and w/c=0.4, and then "computationally hydrated" under saturated and sealed conditions. In the case of sealed (self-desiccating) conditions, the computer model creates empty pore space as the hydration occurs to account directly for the chemical shrinkage. A previous calibration of model cycles to real time (Bentz, 1996) was then applied to create model degree of hydration vs. time curves to compare to the experimental counterparts. In addition, two-dimensional slices from the "fully hydrated" three-dimensional computer model microstructures were created to compare to the SEM images for the two curing conditions for Cement 115 with w/c=0.3.

RESULTS

Saturated and Sealed Specimens

Figure 1 shows a comparison of degree of hydration achieved under saturated and sealed conditions for the two cements studied, with w/c=0.3. In both cases, the sealed conditions are observed to reduce the achieved hydration, particularly at times exceeding 7 days (168 hours). At early times, the newly created empty porosity (from the chemical shrinkage) has only a minor effect on the hydration kinetics as a significant volume fraction of water-filled capillary pore space still exists. For a w/c=0.3 system, initially, about one half of the volume is filled with water. However, as more and more water is consumed by the hydration reactions, the fraction of empty pore space relative to that which is water-filled becomes significant, and a substantial reduction in the hydration rate is observed. The predicted results based on the NIST cement paste microstructural model are seen to closely follow the experimental values, particularly for Cement 115. Thus, it appears that the model is able to account successfully for the effects of self-dessication on hydration kinetics and may be useful as a predictive tool for anticipating the effects of different curing regimens on achievable hydration and physical properties, as the model has already been applied to predicting 7 and 28-day compressive strengths from 3-day values (Bentz, 1996).

It should also be noted that simulations performed for w/c=0.4 for the two cements have indicated much smaller differences in the hydration kinetics for saturated and sealed conditions. For Cement 115, the "final" achieved degrees of hydration after 5000 cycles of the hydration model were 0.88 and 0.83 for the saturated and sealed conditions, respectively. The corresponding values for Cement 116 were 0.90 and 0.85. In addition, the differences to be expected after 28 days of curing, for example, were less than for the w/c=0.3 systems (on the order of 0.01 for Cement 115 and 0.03 for Cement 116). Thus, the effects of sealed curing become more prominent at lower w/c (< 0.4) ratios.

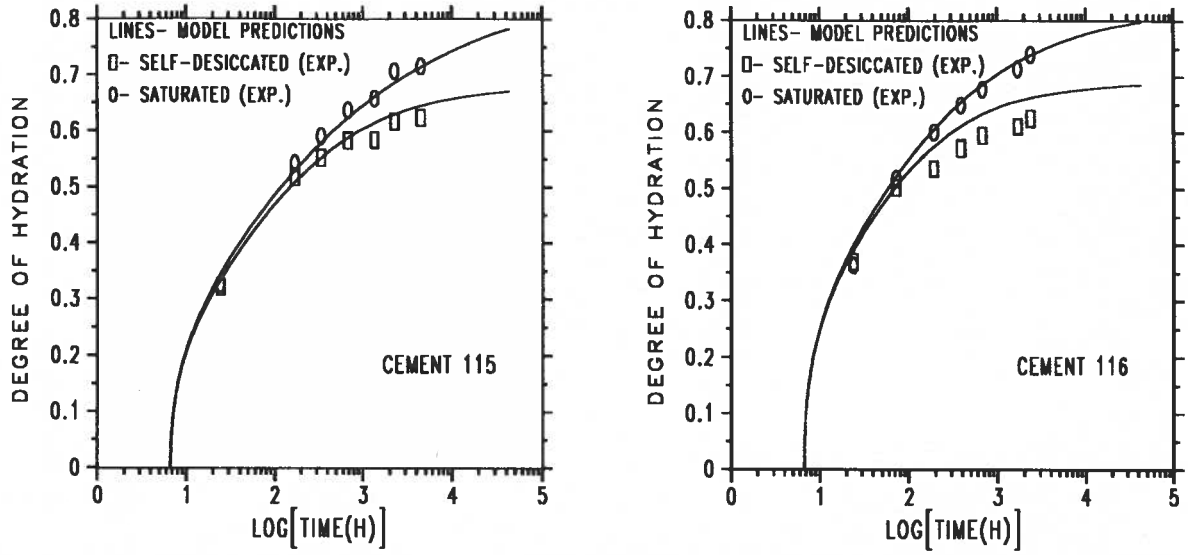

Figure 1: Comparison of saturated and sealed (self-dessicated) hydration for Cements 115 and 116 with w/c=0.3.

Microstructure

The model can be further validated against experiment by comparing SEM micrographs of real sample microstructures to two-dimensional images from the 3-D model. Figures 2 and 3 provide a comparison at similar scales for Cement 115. The two most distinguishing features between the sealed and saturated specimens are the amount and size of the unhydrated cement grains and the amount and size of the observable capillary pores. One can clearly observe that there are more and larger unhydrated cement grains in the sealed specimens (particularly in terms of the alite grains which are surrounded by a dense layer of calcium silcate hydrate gel), in agreement with their measured lower degrees of hydration. Based on quantitative SEM measurements of the unhydrated cement area fractions, after 94 days, the saturated sample has achieved a degree of hydration of 0.79 ± 0.03 while the sealed sample has only achieved a value of 0.66 ± 0.04, based on the averages from eleven fields of view (1024 pixels $\times$800 pixels, 0.25 μm/pixel) for each sample, and expressed with an uncertainty of one standard deviation. By constrast, the corresponding degrees of hydration for the two model systems shown are 0.80 and 0.69, respectively. In addition, due to the emptying of the capillary pores during chemical shrinkage, many relatively larges pores remain in the sealed specimens. Once again, the effects observed in the real specimens are quite accurately duplicated by the model, as the real and model images exhibit many similar features.

Curing Under 90% RH

The results for the effect of the 90% RH environment on cement paste hydration are given in Fig 4. For the case of w/c=0.4, the 6 hour, 12 hour, and 3 day specimens show an effect due to hydration at 90% RH, while the 7 day specimen, over the first 28 days, does not appear to be affected by the change in environment. The data for the 0.3 w/c paste are similar, with the exception that the 3 day specimen also appears to be relatively unaffected by the change in environment.

These data, coupled with an understanding of the percolation of the capillary pore space, lead to a possible explanation for these effects. As the paste hydrates, the capillary porosity, and the characteristic capillary pore size, decrease. When the capillary porosity has been

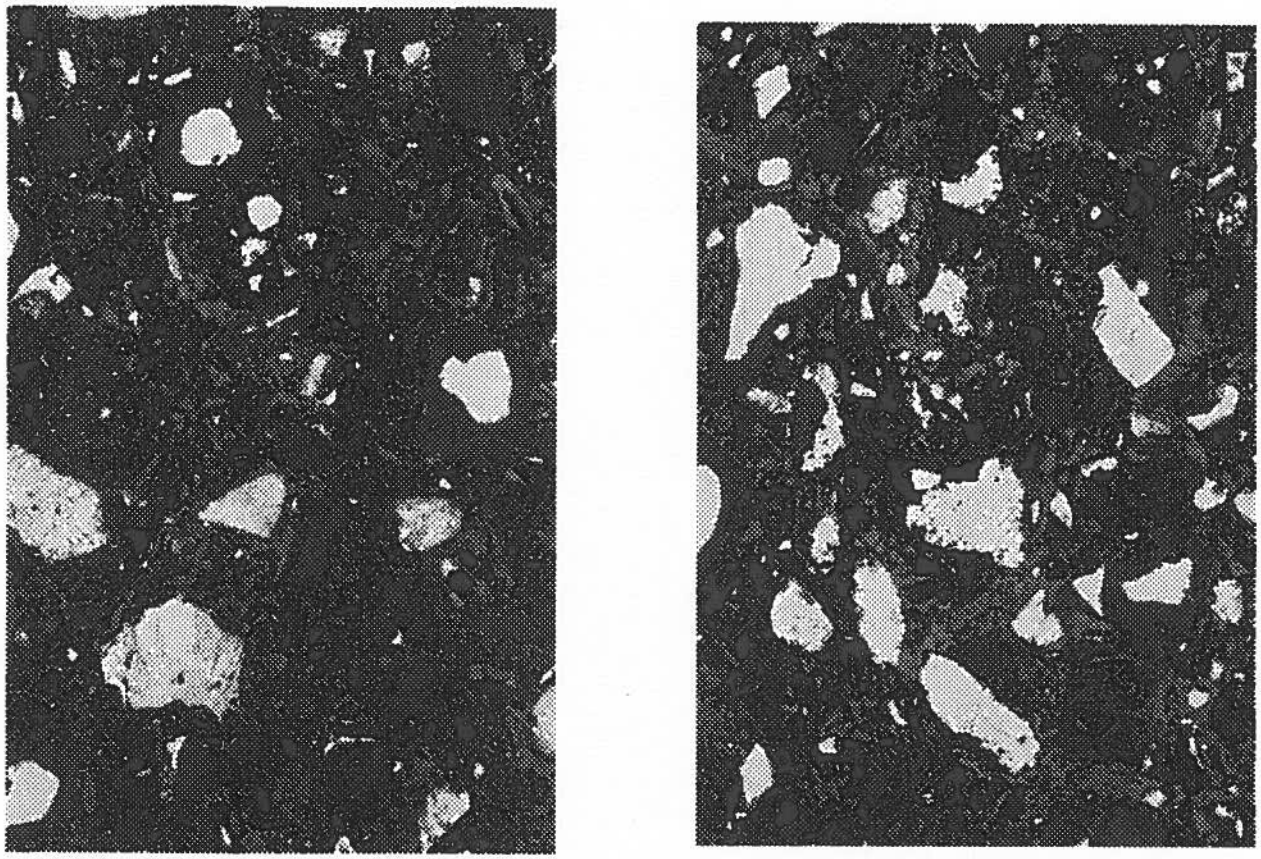

Figure 2: Comparison of real SEM images for saturated (left) and sealed (right) hydration for Cement 115 with w/c=0.3. Unhydrated cement is white, porosity is black, calcium hydroxide is light grey, and calcium silicate hydrate gel and other hydration products are dark grey. Areas imaged are approximately 128 μm $\times$190 μm.

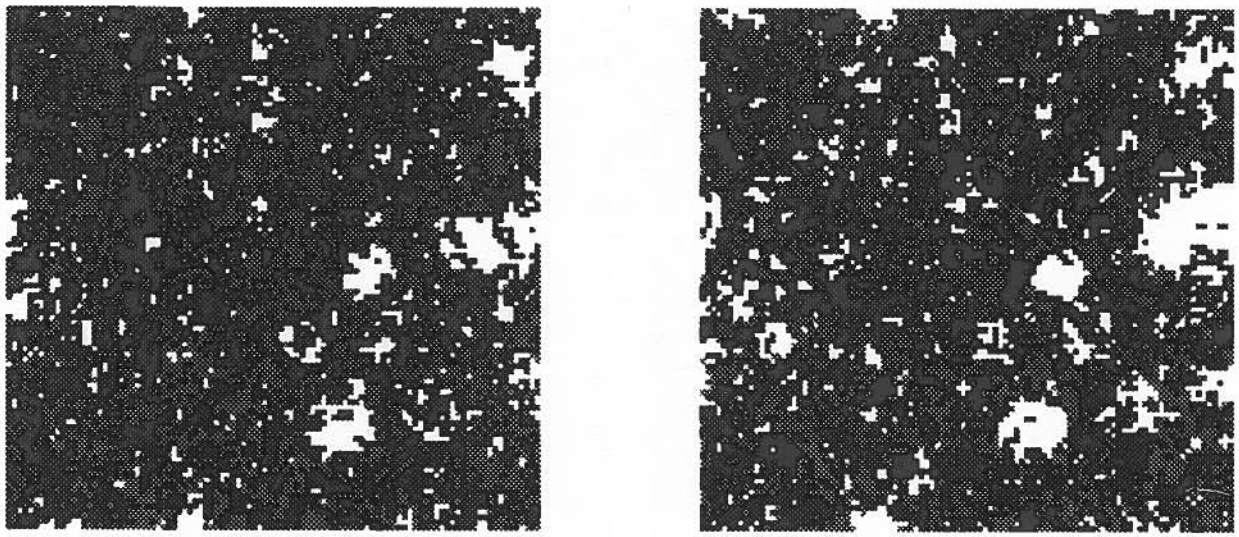

Figure 3: Comparison of model images for saturated (left) and sealed (right) hydration for Cement 115 with w/c=0.3. Greyscale assignments are the same as those given above for the real images. Areas represented by the images are 100 μm $\times$100 μm.

reduced to approximately 0.20, the capillary pore space is no longer interconnected throughout the paste (Powers *et al.*, 1959, and Bentz and Garboczi, 1991). When this occurs, vapor and moisture transport is restricted by the gel pore space, greatly reducing the transport coefficients. These gel pores, due to their small size (< 10 nm in diameter), will remain water-filled at RH values down to about 50% (Baroghel-Bouny, 1994). Any capillary pores connected to the exterior environment only via a path containing gel pores will also remain water-filled at RH > 50%. Thus, when the capillary pore space is no longer percolated, the moisture is, in effect, trapped inside the specimen, and if the specimen is placed in an environment at less than 100% RH, but greater than 50% RH, the specimen continues to hydrate. The estimated degrees of hydration needed to achieve a capillary porosity of 20% are 0.63 and 0.43 for the 0.4 and the 0.3 w/c pastes, respectively, as illustrated by the horizontal dotted lines in Fig 4.

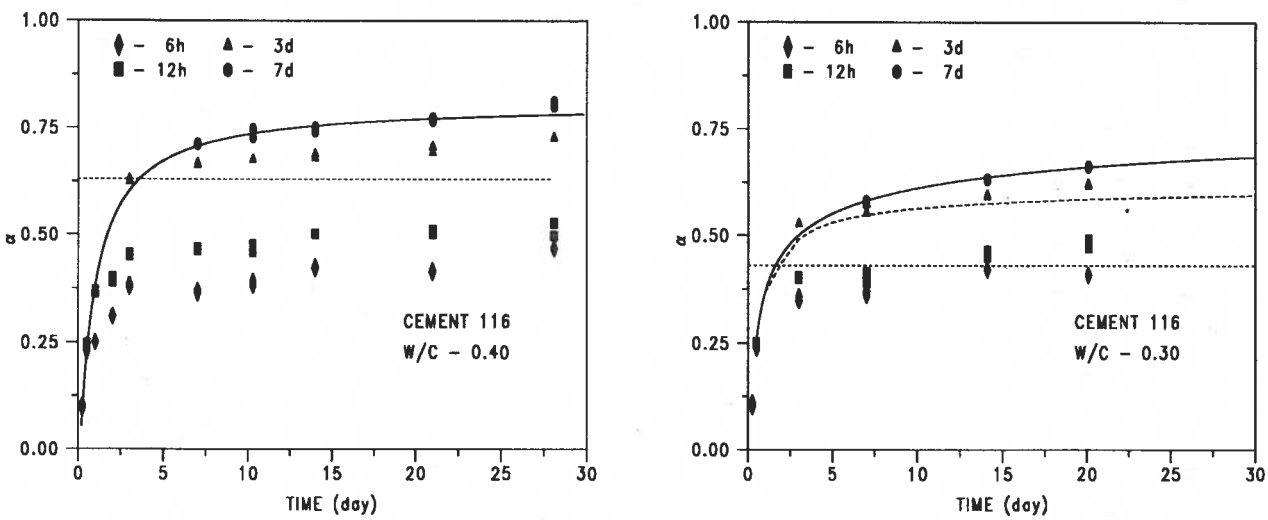

Figure 4: Effect of a 90% RH environment on the degree of hydration (α) for 0.4 and 0.3 w/c cement pastes after curing in 100% RH for 6 and 12 hours, and 3 and 7 days. The solid line indicates continuous hydration at 100% RH, the horizontal dotted line indicates the degree of hydration at which the paste achieves 20% capillary porosity, and the dashed line indicates hydration under sealed conditions for w/c=0.3.

For the w/c=0.3 data, while the 7-day data appear to directly track the saturated condition hydration data, the 3-day data fall slightly below this curve. This might be expected, since after 3 days exposure to 100% RH, the 3-day specimen is then exposed to 90% RH, where even if the capillary porosity has depercolated so that no water is removed, the hydration is continuing under sealed, as opposed to saturated, conditions. As hydration slowly continues beyond 3 days, this will lead to the creation of some empty capillary pores in the specimen due to the chemical shrinkage. Thus, the measured degrees of hydration are seen to fall between the curves for hydration under totally saturated and totally sealed conditions. Conversely, for w/c=0.4, where the saturated and sealed curves will nearly overlap (according to the computer model results discussed earlier), the 3-day system is not able to achieve the performance of a sealed environment. In this case, 7 days of curing are required to equal the performance of a sealed system.

In terms of practical implications, it may be important to realize that when the capillary

porosity depercolates, not only is it more difficult to remove water from the capillary pores in the specimen, but it is also more difficult to maintain saturation of the specimen via an external source of water. This effect has been observed during chemical shrinkage measurements on low w/c ratio cement pastes, where hydration as quantified by chemical shrinkage eventually falls below that measured by non-evaporable water content, as water can no longer be drawn into the specimen at a rate fast enough to maintain saturation (Powers, 1947, Geiker, 1983, and Bentz, 1996). This would imply that extended moist curing would be of limited benefit. However, moist curing during the first two to three days of hydration may be extremely important in maintaining internal saturated conditions to promote hydration, until depercolation of the capillary porosity is achieved. The situation will be even more complex in a concrete than in the cement paste specimens used in this study, due to the presence of the higher porosity interfacial transition zones surrounding each aggregate (Scrivener and Gartner, 1988). It is possible that when the capillary porosity depercolates in the "bulk" paste regions of the concrete, it may still remain interconnected in the interfacial zone paste regions (Winslow *et al.*, 1994 and Scrivener and Nemati, 1996). In this case, prolonged moist curing might be more valuable for a concrete than it would be for a cement paste specimen; more experimental measurements will be necessary to quantify the magnitude of this effect.

CONCLUSIONS

It has been shown that curing environments can have a significant effect on cement hydration kinetics. Even exposure to a 90% RH environment, after 6 or 12 hours of curing at 100% RH, can effectively terminate the hydration process as all remaining capillary water is removed from the specimen. While curing under sealed conditions may be adequate for systems with w/c ratios greater than 0.4, for lower w/c ratios, a significant reduction in the achieved degree of hydration has been observed. The best curing practice, similar to that originally suggested by Powers (Powers, 1947), may be to maintain surface saturated conditions until the capillary porosity depercolates, which will occur at different curing ages for different w/c ratios, and then seal the surface to prevent any moisture loss. The NIST cement paste hydration and microstructural model has provided valuable insights into the effects of sealed conditions and the resultant chemical shrinkage on hydration kinetics and microstructure.

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