Introduction

This chapter presents a review of the application of computational modeling to understanding issues relevant to and predicting performance of systems with internal water curing. Model results are compared to available experimental data and supported by fundamental theories and mechanisms (as outlined in the other chapters of this report).

Two main classes of models are presented: 1) those developed to support the justification for the usage of internal water curing in low water-to-binder ratio \((w/b)\) cement-based materials and 2) those developed to support the application of internal water curing to concrete mixture proportioning. The former of these addresses the question “Why is internal water curing needed?” while the latter pertains to the question “How should internal water curing be applied?”

Models to support justification for internal water curing

Internal water curing provides a means to supply hydrating cement paste with needed curing water when conventional external curing is ineffective, usually due to the lower \(w/b\) of the binder matrix in the concrete. When this needed water is unavailable, self-desiccation will occur, with the formation of a system of (large) empty pores within the cement paste microstructure (see Figure 2 for example). Concurrently, the increase in capillary depression in the capillary pore water may result in a measurable autogenous shrinkage and possible cracking of the sample. The deficiency in water will also result in a measurable decrease in the ongoing hydration rate and possibly strength development. These various effects can be modeled using existing microstructure models, such as CEMHYD3D \([1, 2]\), HYMOSTRUC \([3, 4, 5]\), and DuCom \([6]\).

Various authors \([7, 8, 9]\) have quantitatively measured the reduction in achieved degree of hydration of samples exposed to sealed as opposed to “saturated” curing conditions, with all other experimental variables being equal. Reductions in measured degrees of hydration of as much as 5 % to 15 % have been observed for low \(w/b\) (0.2 to 0.4) cement and blended cement pastes cured for long periods of time (28 d to 150 d). As indicated in Figure 1, microstructural model predictions and experimental measurements are in generally good agreement. In Figure 1, model results are presented for saturated, sealed, and saturated/sealed curing conditions; in the latter case, all pores remain saturated until the capillary porosity in the 3-D microstructural model depercolates, at which point sealed curing conditions are initiated \([8]\).

In addition to a measurable difference in degree of hydration, sealed curing will also dramatically influence the microstructural development of the cement paste. As an example, Figure 2 provides real and model (CEMHYD3D) two-dimensional (from 3-D microstructures) images of a cement paste made with a water-to-cement ratio \(w/c=0.30\) and hydrated under...
saturated and sealed curing conditions for 90 days at 25 °C. It is clear that there are more unhydrated cement particles and more and larger capillary pores in the systems hydrated under sealed conditions. In the CEMHYD3D model under sealed curing conditions, empty capillary porosity is created during the hydration simulation to exactly match the volume formed due to the chemical shrinkage present from the various hydration reactions. To simulate the physical reality, pore “sizes” are assessed locally and the largest pores are emptied first regardless of their location within the cement paste microstructure. X-ray absorption measurements have indeed verified that at early ages, small (5 mm thick) cement paste samples dry out “uniformly” as opposed to developing a sharp drying front [10]. The pore sizes and permeability of the fresh (young) cement paste are such that the capillary water can quickly flow to keep the smaller pores filled at the expense of the larger ones. Of course, these phenomena are also of fundamental importance for the technological application of internal water curing. In internal water curing, the water sources are shifted from being the largest pores in the hydrating cement paste to being the water reservoirs in a special internal water curing agent such as saturated lightweight aggregates (LWA) or superabsorbent polymer (SAP) particles.

In addition to modeling microstructural development under sealed curing conditions, it is also of interest to model the development of the internal relative humidity, as this parameter is an indicator of the magnitude of the stresses developed in the pore fluid and consequently in the solid cement-based material [11, 12]. Neglecting the influence of dissolved salts [12], the Kelvin-Laplace equation quantifies this relation:

\[
\sigma_{cap} = \frac{-2\gamma}{r} = \frac{\ln(RH)RT}{V_m}
\]

where \(\sigma_{cap}\) = capillary stress (N/m²), \(\gamma\) = surface tension of pore solution (N/m), \(r\) = pore radius (m), \(RH\) = relative humidity (0 to 1), \(R\) = universal gas constant (8.314 J/mol-K), \(T\) = absolute temperature (K), and \(V_m\) = molar volume of water (m³/mol).
Figure 2: Scanning electron microscopy (SEM) (top) and CEMHYD3D model (bottom) images for saturated (left) and sealed (right) hydration of a $w/c=0.30$ cement paste after curing at 25 °C for 90 d [8]. SEM images are 128 µm by 190 µm; model images are 100 µm by 100 µm. Phases from brightest to darkest are: unhydrated cement, calcium hydroxide, calcium silicate hydrate gel, and porosity (empty and water-filled).
Based on measured desorption isotherms, Norling Mjörnell has developed a detailed model for predicting degree of hydration and internal relative humidity in ordinary and high-performance concretes [9]. By assuming the following cumulative pore size distribution, as opposed to measuring the desorption isotherms, van Breugel and Koenders [3, 4] have modeled the reduction in internal relative humidity with increasing hydration time in cement-based materials, as exemplified by the results presented in Figure 3.

\[
\frac{V_{\text{por}}}{V} = a \ln\left(\frac{\phi_{\text{por}}}{\phi_0}\right) \tag{2}
\]

where \(V_{\text{por}}\) = cumulative pore volume in the paste for pores of diameter \(\phi_{\text{por}}\) and smaller (m³), \(V\) = the total volume of the paste system (m³), \(\phi_{\text{por}}\) = pore diameter (nm), \(\phi_0\) = the diameter of the smallest pore in the system = 2 nm, and \(a\) = pore structure constant based on experimental data (typically 0.05 to 0.15) [4]. Ye has extended the HYMOSTRUC model to provide an even more realistic pore size distribution curve, as shown in Figure 4 [5].

![Figure 3: (a) Schematic representation of cumulative pore size distribution indicating that largest pores empty first during self-desiccation; (b) Modeled relative humidity versus the degree of hydration for three different w/c (wcr) and three different finenesses of cement.](image)

Based on the diameter of the largest water-filled pore in the system, from equation (2) or from a computed pore size distribution such as that in Figure 4b, the relative humidity and capillary stress in the system can be calculated using the Kelvin-Laplace equation (1). Differences in the fineness of the cement cause differences in the formation of the microstructure and lead inherently to changes in the refinement of the pore structure [3, 4, 11]. From the Kelvin-Laplace equation, it can be observed that the relative humidity in the system is directly related to a pore radius. The development of a low relative humidity can thus be opposed by internal water curing, as the largest water-filled pores are shifted from being the larger pores in the hydrating cement paste to being the pores located in the supplied water reservoirs.
One microstructural component where a large influence of curing conditions may be observed is in the interfacial transition zone (ITZ) regions surrounding each aggregate (and air void, etc.) in concrete [4, 13, 14, 15]. Because of inefficient packing of the cement particles in the immediate vicinity of the aggregate (the “wall effect”), often there will be larger and more capillary pores in the ITZ, due to its initially higher local w/c ratio, as illustrated in Figure 5a [15]. Thus, particularly for low w/c pastes, the ITZs can behave as water sources for the desiccating bulk cement paste matrix. During sealed curing conditions, these larger pores in the ITZs will likely be the first to empty as indicated by the two-dimensional images in Figure 6 and the plots of empty porosity vs. distance from the aggregate surface in Figures 7 and 8, for simulations conducted using both the CEMHYD3D and the HYMOSTRUC microstructure models. The influences of cement particle size, w/c, and curing conditions are all clearly observed.
Figure 6- Simulated initial (top) and “completely” hydrated (bottom) ITZ microstructures for cements with median diameters of 5 µm (left) and 30 µm (right) and a w/c=0.30 [13]. Images are 100 µm by 100 µm. Hydration conducted under sealed conditions at 25 °C. In the initial images, phases from brightest to darkest are: C₃S, C₂S, C₃A, C₄AF, gypsum, and porosity. In the hydrated images, phases from brightest to darkest are: unhydrated cement, calcium hydroxide and other hydration products, calcium silicate hydrate gel, and porosity. Central bar extending across the microstructure is the flat plate aggregate.

It should be noted that because the smaller cement grains tend to concentrate in the ITZ region (Figure 6) and because the achieved degree of hydration in the ITZ regions can be significantly higher than that in the bulk paste (Figure 5b), the preferential movement of water from ITZ to bulk paste during hydration under sealed conditions is not guaranteed, but will depend on the specific characteristics of the system being considered (w/c, particle size distribution, etc.). However, because in a sealed system the self-desiccation process begins with the setting of the cement, it is likely that the very first pores to empty will be in the ITZ regions. At these early ages, the enhanced hydration in the ITZ relative to the bulk paste will not yet have a significant influence on local pore sizes (DOH = 0.274 curve in Figure 5b). The situation becomes even more complex in the presence of internal water curing. For example, if partially
unsaturated LWA are added to the concrete mixture for internal water curing, their initial further absorption of mixing water could significantly densify the local ITZ microstructures [14]. Of course, in this case, it is intended that the pores in the LWA and not those in the ITZ will be the first to empty during hydration.

![Figure 7: Empty porosity (fraction of total paste volume) as a function of distance from the aggregate surface for CEMHYD3D hydrated cement pastes with two different particle size distributions (5 µm and 30 µm), two different curing conditions (sealed and saturated/sealed), and \( w/c = 0.3 \) [13].](image1)

![Figure 8: Empty porosity (empty porosity/total porosity) as a function of the distance from the aggregate surface for HYMOISTRUC hydrated cement pastes with three different \( w/c \).](image2)
Models to support application of internal water curing

There are at least three basic questions that one can ask when considering mixture proportioning for internal water curing: 1) How much extra internal curing water needs to be supplied for a given concrete?, 2) How far can the water effectively travel from its reservoir (source)?, and 3) How is the internal curing water (or its reservoirs) distributed within the concrete microstructure? Each of these questions can be addressed using one or more computational modeling approaches. Many of the models discussed in this section are executable at an internal curing web site at http://ciks.cbt.nist.gov/lwagg.html.

How much water?

Powers’ model for hydrating cement paste provides an effective means of addressing the first question [16]. In chapter 3 (Mechanisms of Internal Water Curing) this issue is treated in detail.

How far can the water travel?

Weber and Reinhardt [17] have presented a detailed analysis of water transport from lightweight aggregates to cement paste. The analysis presented below is a variant inspired by their approach, in which the water flow rate is equated to the value needed to maintain saturation in the hydrating cement paste. It is assumed that the cement paste and water reservoirs are both composed of a set of equi-size cylindrical pores as shown in Figure 9. In the case of the water reservoirs, the pore size is fixed while in the case of cement paste, the pore size decreases with continuing hydration. In this simplified model, the only flow considered is that from the LWA pores to the hydrating cement paste pores due to the pressure differential between them.

We begin by considering the flow of water through a cylindrical pore (radius $R_{paste}$ and length $L$, both in units of m) in the hydrating cement paste in a unit volume ($1 \text{ m}^3$) of concrete. The volumetric flow in $\text{m}^3/s$, $Q$, is given by:

$$Q = -\frac{\pi R_{paste}^4 \Delta P}{8 \mu L} = -\frac{\pi R_{paste}^2 k \Delta P}{\mu L} \quad \text{with} \quad k = \frac{R_{paste}^2}{8}$$

(3)

where $\Delta P = \text{pressure drop (Pa)}$, $k = \text{permeability (m}^2\text{)}$, and $\mu = \text{fluid viscosity (0.001002 Pa}\cdot\text{s for water at 20 °C)}$. If water is flowing from a pore of radius $R_{res}$ (m) in the water reservoir (effectively creating a meniscus within this reservoir pore) into a pore of radius $R_{paste}$ in the hydrating cement paste, the pressure drop can be estimated by [17]:

$$\Delta P = \frac{2\gamma}{R_{res}} - \frac{2\gamma}{R_{paste}}$$

(4)

where $\gamma$ is the surface tension of water (0.07275 Pa•m at 20 °C) and a contact angle of 0 degrees has been assumed. $R_{paste}$ should logically be the largest pore size in the cement paste that desires to be water-filled at the expense of the pores in the water reservoirs.
Figure 9: Schematic representation of pores in water reservoirs and cement paste for water flow distance model (not to scale).

It is desirable that this water flow exactly balance the water demand of the concrete due to the ongoing chemical shrinkage. We define a fill factor, $\frac{\partial \varepsilon}{\partial t}$, as the water demand per unit volume of concrete porosity (units of $s^{-1}$) to maintain saturation. This will be given by the differential rate of water demand on a volumetric basis, divided by the capillary porosity of the concrete, $\Phi_{\text{concrete}}$ or:

$$\frac{\partial \varepsilon_i}{\partial t} = \frac{CS(\frac{\partial \alpha}{\partial t})C_f}{\rho_w \Phi_{\text{concrete}}}$$

(5)

where $\frac{\partial \alpha}{\partial t}$ is the current hydration rate for the time period of interest ($s^{-1}$) and $\rho_w$ is the density of water (998.23 kg/m$^3$ at 20 °C). Then, extending equation (5) from a global porosity to a local individual pore level, we require that our volumetric flow rate within the individual pores, $Q$, also be:
Finally, equating equations (3) and (6), and solving for $L$ yields:

$$L = \sqrt{\frac{k|\Delta P|}{\mu \frac{\partial \varepsilon_l}{\partial t}}}$$

With estimates of the permeability of the cement paste [18] and the pore sizes of the paste and water reservoirs, one can calculate first the pressure and then the pore length or water flow distance. Here, a pore radius of 10 µm was selected for the water reservoirs, but using a value of 100 µm, for example, resulted in only minor changes in the calculated flow distance values presented in Table I, which provides the calculated pore lengths (or water flow distances) for early, middle, late, and “worst case” hydration conditions for low w/b cement paste in concrete.

Table I: Calculated water flow distances in cement pastes of various ages with the water reservoir pore radius set at 10 µm, chemical shrinkage ($CS$) of 0.07 kg water/kg cement and a cement factor ($C_f$) of 700 kg/m$^3$.

<table>
<thead>
<tr>
<th>Age</th>
<th>Paste permeability (m$^2$) [18]</th>
<th>$R_{\text{paste}}$ (m)</th>
<th>$\Delta P$ (Pa)</th>
<th>Hydration rate $\frac{\partial \varepsilon_l}{\partial t}$ (s$^{-1}$)</th>
<th>Concrete porosity $\Phi_{\text{concrete}}$</th>
<th>Fill fraction $\frac{\partial \varepsilon_l}{\partial t}$ (s$^{-1}$)</th>
<th>Flow distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early</td>
<td>1.00E-17</td>
<td>1.0E-06</td>
<td>-130950</td>
<td>6.94E-06</td>
<td>0.12</td>
<td>2.84E-06</td>
<td>21.4</td>
</tr>
<tr>
<td>middle</td>
<td>1.00E-20</td>
<td>1.0E-07</td>
<td>-1440450</td>
<td>1.16E-06</td>
<td>0.06</td>
<td>9.47E-07</td>
<td>3.90</td>
</tr>
<tr>
<td>Late</td>
<td>1.00E-22</td>
<td>2.00E-08</td>
<td>-7260450</td>
<td>2.31E-07</td>
<td>0.015</td>
<td>7.58E-07</td>
<td>0.98</td>
</tr>
<tr>
<td>worst</td>
<td>1.00E-23</td>
<td>2.00E-08</td>
<td>-7260450</td>
<td>2.31E-07</td>
<td>0.01</td>
<td>1.14E-06</td>
<td>0.25</td>
</tr>
</tbody>
</table>

One can observe that the “likely” water flow distances vary from tens of millimeters at early ages to millimeters at middle ages to hundreds of micrometers at later ages. While these estimates are quite approximate in nature due to high uncertainties in the proper values to use for paste permeability and pore radius, the early and middle age flow distances are quite similar to the observed penetration depths of drying fronts in a w/c=0.40 ordinary portland cement paste, based on X-ray absorption measurements [19]. In that study, a penetration depth on the order of 20 mm was observed for specimens immediately exposed to a drying environment while a penetration depth of about 4 mm was observed for specimens first cured under saturated conditions for 1 d or 3 d. Penetration depths of several millimeters during the first few days of sealed curing, as predicted for middle age (Table I), were reported in [20] based on a combined experimental and analytical evaluation.

How is the internal curing water distributed within the three-dimensional concrete?

Knowing how much internal curing water is needed and how far the water can reasonably travel within the cement paste, the final piece of the puzzle is how the water reservoirs are distributed in the three-dimensional concrete microstructure. A proper analogy for this question is that of the protected paste volume concept for air-entrained concrete [21, 22]. Instead of being
interested in what fraction of the cement paste is within a given distance of an air void, here we are concerned with what fraction of the cement paste is within a given distance of a water reservoir. This analogy may actually apply in both directions, as empty water reservoirs may serve as an effective air entrainment system [21, 23].

A three-dimensional hard core/soft shell microstructure model can be conveniently applied to determining the “protected” paste volume as a function of distance from a water reservoir (LWA or SAP). Such a model has been developed at NIST and is available for free downloading at http://ciks.cbt.nist.gov/cmml.html [24] or for execution over the Internet at http://ciks.cbt.nist.gov/lwagg.html. Similar models have been employed by other research groups [20]. Basically, a three-dimensional volume of concrete is represented as a continuum three-dimensional cube filled with solid aggregate (or SAP) particles. Both particles that supply water and those that do not are considered in the most general formulation of the computer model. Generally, in models of this type, water absorption by the normal weight aggregates is not considered, thus representing a worst-case scenario with regards to internal water curing. The “hard core” particles are placed at random locations from largest to smallest such that they do not overlap one another. Water reservoir particles are then surrounded by “soft shells” of various thicknesses and the volume fraction of the matrix cement paste as a function of shell thickness is computed using systematic 3-D point sampling [24]. The general output of the model consists of a table of the protected paste volume as a function of distance from the water reservoir surface and a two-dimensional color-coded image illustrating the availability of water within the concrete microstructure. Typical results are provided in Figure 10 and Table II for a concrete with 70 % aggregates by volume and replacement of 20 % of the fine aggregates by water reservoirs. In this example, 100 % of the cement paste is within 1.0 mm of a water reservoir surface (a relevant distance for early and middle age curing) and 98 % of the cement paste is within 0.5 mm (a more relevant distance for later age curing) [25].

Figure 10: Example two-dimensional image (1.6 cm x 1.6 cm) from a portion of an internal water curing simulation [25].
Table II: “Protected Paste” Volume vs. Distance from the Water Reservoir Surfaces

<table>
<thead>
<tr>
<th>Distance from Water Reservoir Surface (mm)</th>
<th>Protected Paste Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.046</td>
</tr>
<tr>
<td>0.05</td>
<td>0.128</td>
</tr>
<tr>
<td>0.1</td>
<td>0.280</td>
</tr>
<tr>
<td>0.2</td>
<td>0.563</td>
</tr>
<tr>
<td>0.5</td>
<td>0.978</td>
</tr>
<tr>
<td>1.0</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Lu and Torquato have developed analytical equations for this same quantity that are strictly applicable for two-phase systems [26]. Concrete with internal water curing is at least a three-phase system, consisting of matrix (cement paste), water reservoirs (LWA or SAP), and normal weight aggregates. Bentz and Snyder [21] have shown that a simple modification of the Lu and Torquato equations to account for the normal weight aggregate volume fraction provides results in reasonable agreement with the three-dimensional simulations for distances up to several hundred micrometers, while Zhutovsky et al. [20] showed that the modified analytical predictions are less accurate when larger flow distances of several millimeters are considered.

As illustrated by Reinhardt and Mönnig [27], models such as DuCom [6] can allow an even more detailed modeling of the water distribution within a concrete with internal water curing. Figure 11 shows an example of the water distribution (in units of kg/m$^3$) in a system with a single initially saturated water reservoir particle in its center (water reservoir volume fraction of 15 % and cement paste w/c=0.33). The top side of the cube (z direction) was open to the atmosphere (20 °C and 65 % RH). The water content is clearly higher in the vicinity of the water reservoir. As illustrated in Figure 12, this results in a concurrent increase in the achieved degree of hydration after 14 d of curing, relative to a system with no internal water curing.

Figure 11: Water distribution in units of kg/m$^3$ simulated with the DuCom model [6, 27].
Figure 12: Degree of hydration vs. saturated lightweight aggregate content of 3-D DuCom microstructures after 14 d \([6, 27]\) of hydration under sealed, one open surface, or two open surface curing conditions with \(w/c=0.33\).

Prospectus

As internal water curing moves from the laboratory into practice, computer modeling can provide an important tool for placing the technology on a strong materials science basis. As with all materials, the most rapid and far reaching advances in the field will be achieved by a tightly interwoven combination of experimental studies and computer modeling. While much remains to be done in both arenas, a strong foundation that will foster understanding and innovation has already been laid.

References:


