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Capillary Porosity Depercolation/Repercolation in Hydrating Cement Pastes Via Low-Temperature Calorimetry Measurements and CEMHYD3D Modeling

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Capillary porosity percolation in a hydrating cement paste has a large influence on transport properties and durability. Percolation can be examined using low-temperature calorimetry and using microstructure models. In this paper, the two approaches are compared for cement pastes with different water-to-cement ratios and exposed to various curing conditions. The influence of sealed curing is seen to be particularly important, as cement pastes that initially hydrate to depercolate the capillary pores may later undergo self-desiccation and aging that repercolates them. Model predictions of the degree of hydration and the percolated capillary porosity volume fraction compare favorably with experiments.

I. Introduction

MANY years ago, Powers *et al.*¹ first noted that during the hydration of portland cement, the capillary porosity could become discontinuous. This depercolation has many implications for the transport properties and durability of cement-based materials. For example, the permeability of a cement paste with a depercolated pore structure can be more than a factor of 1000 less than an equivalent age (higher water-to-cement mass ratio [w/c]) paste with a pore structure that remains percolated.² The stability of the depercolated pore structure is of equal importance to its initial depercolation. Powers *et al.*² indicated that the simple slow drying of a cement paste to an equilibrium relative humidity of 79% could increase its permeability by a factor of about 70.

While X-ray computed microtomography is now approaching spatial resolutions of better than 1 μm , by which the three-dimensional percolation of the capillary pore structure in hydrating cement paste can be directly observed,³ conventionally, percolation/depercolation has been inferred indirectly from measurements of chemical shrinkage^{4,5} or low-temperature calorimetry (LTC) scans.^{6,7} In addition, capillary porosity percolation has been predicted using the National Institute of Standards and Technology (NIST, Gaithersburg, MD) CEMHYD3D hydration and microstructure development computer model.^{8,9} In this paper, capillary porosity depercolation/repercolation in hydrating cement paste is investigated as a function of w/c (0.25–0.45), curing temperature (20° or 40°C), and saturation (saturated or sealed curing), from both an experimental and a computer modeling point of view.

II. Experimental Procedure

(1) Specimen Preparation

The cement pastes analyzed in this study were prepared using Cement and Concrete Reference Laboratory (CCRL) portland

cement proficiency sample 152,¹⁰ issued in January 2004. Its particle size distribution, as measured by laser diffraction, is provided in Fig. 1. By volume, the cement contains 69.0% tricalcium silicate, 8.8% dicalcium silicate, 12.3% tricalcium aluminate, and 3.8% tetracalcium aluminoferrite. Additionally, it contains 6% calcium sulfates by volume fraction, distributed as approximately 44% gypsum (calcium sulfate dihydrate), 52% hemihydrate, and 4% anhydrite, as determined by X-ray diffraction measurements. Cement pastes with initial $w/c = 0.35$ and 0.45 on a mass basis were prepared by mixing for several minutes at either 20° or 40°C in a temperature-controlled high-speed blender. For the more viscous $w/c = 0.25$ cement pastes, mixing was performed by kneading the paste by hand in a sealed plastic bag. Cast wafers (≈ 5 g) of the prepared pastes, approximately 32 mm in diameter and 2–5 mm in thickness, were placed in small, capped plastic vials to be cured at either 20° or 40°C. After about 4 h of curing, any accumulated bleed water was removed from the vials using a pipette, to assess the “true” effective w/c of the pastes. While all of the $w/c = 0.25$ and 0.35 cement pastes cured at either 20° or 40°C, as well as the $w/c = 0.45$ cement pastes cured at 40°C, contained negligible bleed water, for the $w/c = 0.45$ pastes cured at 20°C, after removing the accumulated bleed water, a paste with an effective $w/c = 0.435$ remained.

With respect to specimen saturation, two curing conditions were used. In saturated curing, a small amount of distilled water was placed on top of the paste wafers after removing the bleed water. In sealed curing, the wafers were simply sealed in their plastic vials after removing the bleed water. The 20°C curing was conducted in a walk-in environmental chamber, while the 40°C curing was conducted in a temperature-controlled water bath. At various ages between 1 and 256 days, wafers were removed from their vials and crushed into small pieces, some of which were retained for the LTC analysis as described below. The remaining pieces were further crushed to a fine powder, flushed with methanol in a thistle tube under vacuum to stop their hydration, and divided between two crucibles (for replicates) for determination of degree of hydration via loss-on-ignition (LOI) measurements as described below.

(2) Degree of Hydration

The non-evaporable water content (w_n) of each crucible sample was determined as the mass loss between 105° and 1000°C divided by the mass of the ignited sample, corrected for the LOI of the unhydrated cement powder, which was determined in a separate LOI measurement. Previously, the expanded uncertainty in the calculated w_n has been estimated to be 0.001 g non-evaporable water/g cement.⁵ The values of w_n were converted to estimated degrees of hydration based on the phase composition of the cement and published coefficients for the non-evaporable water contents of the various cement clinker phases.¹¹ Based on a propagation of error analysis, the estimated uncertainty in the calculated degree of hydration is 0.004.

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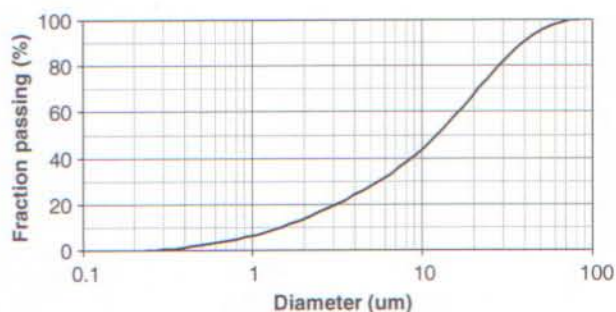


Fig. 1. Measured cumulative particle size distribution for Cement and Concrete Reference Laboratory cement 152.

(3) LTC

Small pieces of the hydrated cement pastes were also used in the LTC experiments. Sample mass was typically between 30 and 90 mg. For each LTC experiment, one small piece of the relevant cement paste was surface dried and placed in a small open stainless-steel pan. The pan with the sample, along with an empty reference pan of mass similar to the empty sample pan, was placed in the calorimeter cell. Using a protocol developed previously,⁶ a freezing scan was conducted between 5° and -55°C at a scan rate of -0.5°C/min. For temperatures between -100° and 500°C, the equipment manufacturer has specified a constant calorimetric sensitivity of $\pm 2.5\%$ and a root mean square baseline noise of 1.5 μ W. For comparison, typical measured signals for a freezing scan are on the order of 0.5–1 mW. The peaks observed in a plot of heat flow (normalized to the mass of the sample) versus temperature correspond to water freezing in pores with various size entryways (pore necks).⁶ The smaller the pore entryway, the more the freezing peak is depressed. Thus, the presence of, absence of, or change in peaks can be used to infer information concerning the characteristic sizes of the “percolated” (connected) water-filled pores in the microstructure of the hydrating cement pastes. Villadsen^{12,13} has demonstrated that when specimens are first dried equivalently (and then resaturated for the LTC measurements), LTC and mercury intrusion porosimetry (MIP) produce similar pore size distributions. However, one advantage of LTC over MIP, and most other techniques for assessing pore size and connectivity, is that specimens can be evaluated without any applied external drying that might damage and modify the pore structure. Of course, the LTC technique can only assess the size and connectivity of water-filled pores. For sealed curing conditions, it is assumed that “empty” pores formed because of self-desiccation will not contain any freezable water and thus will not show up on the LTC scans. For this reason, many of the specimens originally cured under sealed conditions were first resaturated for 1 day or more and then analyzed using the LTC technique. It is recognized that the sealed curing and its accompanying internal drying (self-desiccation) can modify the microstructure in a manner analogous to drying.^{7,14}

III. Microstructural Modeling

All microstructural modeling was conducted using version 3.0 of the CEMHYD3D software (<ftp://ftp.nist.gov/pub/bfrl/bentz/CEMHYD3D/version30>).¹⁵ Starting microstructures, with a spatial resolution of 1 μ m, were created to match the four different w/c values (0.25, 0.35, 0.435, and 0.45) used in the experiments. For each starting microstructure, isothermal hydration was conducted for the various curing conditions used in the experiments, generally consisting of two different hydration temperatures (20° or 40°C) and two saturations (saturated or sealed curing). The main computer model outputs of interest for this study include the achieved degree of hydration and the percolation (fraction) of the capillary porosity as a function of time. The achieved experimental degree of hydration data was used to

Table I. Comparison of CEMHYD3D and CCRL Proficiency Sample Program ASTM C186 Heat of Hydration Test Method Results¹⁶

Age (days)	CEMHYD3D heat of hydration (J/g)	CCRL measured heat of hydration (J/g)	CCRL measured standard deviation (J/g)
7	372.8	362.8	30.96
28	420.3	415.0	23.85

CCRL, Cement and Concrete Reference Laboratory.

calibrate the kinetic factor in the microstructural model. Then, this same calibration factor was used for all hydration simulations (both temperatures and curing conditions) and the model results for percolated capillary porosity fraction were also compared with the experimental results from the LTC curves. For all results presented in this paper, a calibrated (curve fitted) kinetic factor of 0.00027 h/(cycle $\times$ cycle) was selected to convert between model hydration cycles and real (experimental) time, and an (Arrhenius-based) activation energy of 45.5 kJ/mol was used for the cement hydration reactions.⁵ This value of the activation energy implies that the cement hydration reactions for cement 152 are initially about 3.3 times faster at 40°C than they are at 20°C.

To further validate this choice of 0.00027 as the kinetic parameter for modeling the hydration of cement 152, two additional starting microstructures were created to simulate the results of the American Society for Testing and Materials (ASTM) C186 heat of hydration and the ASTM C109 mortar cube compressive strength tests,¹⁶ respectively, conducted in the CCRL proficiency sample testing program.¹⁶ In the first case, a starting microstructure with $w/c = 0.4$ was created and hydrated under sealed curing conditions at 23°C, in accordance with the ASTM C186 test method.¹⁶ Using the same kinetic parameter given above, the CEMHYD3D model values for heat of hydration after 7 and 28 days of hydration were determined for comparison with the experimentally determined values, as summarized in Table I. Excellent agreement was observed between the CEMHYD3D predictions and the measured values of heat of hydration for this particular cement, with the difference between model and experimental values being within 33% of the standard deviation measured in the CCRL proficiency sample program.

In the second case, a $w/c = 0.485$ starting microstructure was created and hydrated under saturated conditions at 23°C, in accordance with the ASTM C109 test method.¹⁶ Compressive strengths were modeled using Power's gel-space ratio,⁵ with an exponent of 2.6 and a strength pre-factor of 99.3 MPa, to obtain agreement with the measured 3 days compressive strength value. The results are plotted in Fig. 2, where it can be seen that the CEMHYD3D strength predictions for 7 and 28 days (based on the 3-day measured value) lie within two standard deviations of the values measured in the CCRL proficiency sample program.

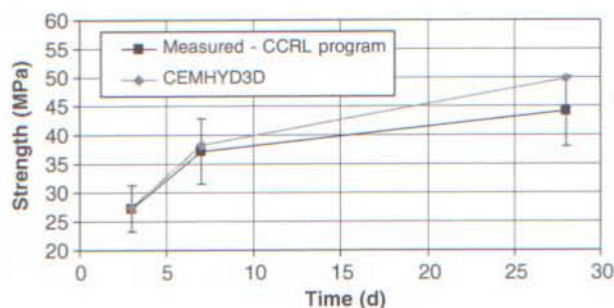


Fig. 2. Comparison of CEMHYD3D predicted and Cement and Concrete Reference Laboratory (CCRL) measured ASTM C109 mortar cube compressive strengths as a function of curing age for CCRL cement 152. Error bars on CCRL program data indicate $\pm$ two standard deviations.

IV. Results and Discussion

(1) Degree of Hydration

To examine the agreement between CEMHYD3D predictions and measured degrees of hydration, the $w/c = 0.35$ cement pastes cured under saturated conditions at 20°C were first selected. The measured and CEMHYD3D predictions for degree of hydration are provided in Fig. 3, and it can be seen that there is nearly perfect agreement between the experimental results from two different sets of specimens (A and B) and those predicted by CEMHYD3D, using the cycle/time conversion factor of $0.00027 \text{ h/cycle}^2$. For the sealed curing results also shown in Fig. 3, it is observed that the CEMHYD3D model underpredicts the hydration achieved in the real specimens at later ages.

Next, the influence of curing temperature on the degree of hydration achieved was examined by considering the $w/c = 0.35$ cement paste cured at 40°C . It has previously been observed that calcium silicate and cement pastes cured at higher temperatures exhibit a coarser pore structure, perhaps because of the formation of a denser calcium silicate hydrate gel (C-S-H) layer around the cement particles.^{17,18} To attempt to better incorporate this effect into version 3.0 of the CEMHYD3D software, a parameter that influences the distance that "diffusing C-S-H" species are located from the initial cement particle surfaces, was varied from its version 2.0 fixed value of 8 (elements) down to 1. In CEMHYD3D,^{5,15} when elements (voxels) of tricalcium silicate or dicalcium silicate are selected for dissolution, the selected element of the original silicate is removed, an element of "diffusing C-S-H" is created at a porosity element immediately adjacent to the dissolution site, and, as needed to maintain the appropriate volume stoichiometry of the hydration reactions, an additional element of diffusing C-S-H is placed at a random location near the original dissolution source, specifically within a $2n \times 2n \times 2n$ cubic (box) volume centered at the dissolution source element. The diffusing C-S-H elements then undergo a random walk diffusion process within the available capillary porosity until precipitating on a solid surface. Decreasing the value of n should indirectly result in a denser layer of C-S-H elements being formed around the unhydrated cement particle cores, leading to a coarser capillary porosity and likely a reduction in the hydration achieved at longer times as well. In version 2.0 of CEMHYD3D, n had a fixed value of 8, while in version 3.0, the value of n has been made to be a function of temperature as described further below. The results for the predicted degree of hydration as a function of n are shown in Fig. 4. Based on these results, the C-S-H location parameter was set to be a linear function of temperature with a value of 3 for all (further) 40°C hydration simulations, while maintaining a value of 8 for the 20°C simulations using

$$n = \text{C-S-H}_{\text{box_size}} \\ = \text{Max} \left[1, \text{int} \left\{ 3 + 5 \frac{(40 - T)}{20} \right\} \right] \quad (1)$$

where Max and int represent the maximum and integer functions, respectively. The influence of n on the percolation prop-

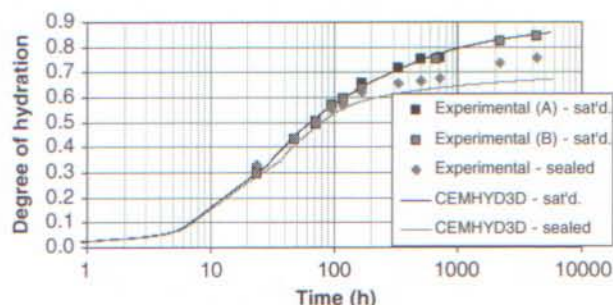


Fig. 3. Measured and CEMHYD3D predicted degree of hydration for $w/c = 0.35$ cement paste cured at 20°C .

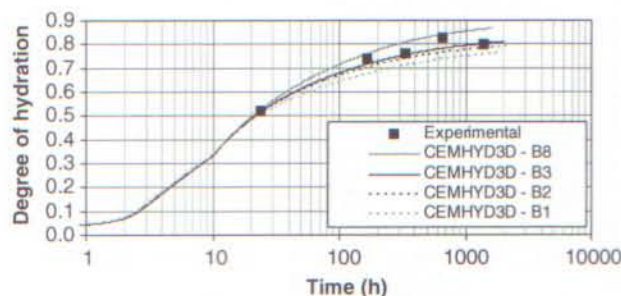


Fig. 4. Measured and CEMHYD3D predicted degree of hydration for $w/c = 0.35$ cement paste cured at 40°C under saturated conditions, as a function of the local box size used for C-S-H precipitation (B1— $n = 1$ voxel to B8— $n = 8$ voxels).

erties of the capillary porosity will be presented subsequently. As shown in Fig. 5, $n = 3$ also provides a good fit of the CEMHYD3D model to the experimental data obtained for the $w/c = 0.35$ cement pastes cured under sealed conditions at 40°C .

Equivalent hydration plots for the $w/c = 0.435$ and 0.45 cement pastes are provided in Figs. 6 and 7, respectively. For these higher w/c ratios, a much smaller influence of saturation (sealed versus saturated) is observed, as sufficient initial water is present to continue the hydration in the sealed samples even as chemical shrinkage and self-desiccation occur.⁷ For all four cases shown in Figs. 6 and 7, the agreement between the experimental measurements and the CEMHYD3D predictions appears reasonable.

Results for the much denser $w/c = 0.25$ cement pastes are presented in Figs. 8 and 9. While the sealed hydration predictions of CEMHYD3D are reasonable for both curing temperatures, the saturated results are surprising in that the LOI-based measured degrees of hydration are much greater than the CEMHYD3D model predictions at later ages, particularly for the 40°C curing. These experimental values even significantly exceed the nominal value for the expected ultimate degree of hydration in a $w/c = 0.25$ cement paste of about $0.25/0.36 = 0.694$. As noted previously by Hansen,¹⁹ it appears that low w/c cement pastes cured at higher temperatures have an inherently higher amount of chemically bound (or at least non-evaporable) water than conventional w/c pastes. When the C-S-H is restricted to form in very confined spaces, it appears that while its physically bound water per unit hydration may decrease, its chemically bound water increases, as has also been observed for densified with small particles (DSP) $w/cm = 0.18$ blended cement pastes hydrated at 23°C under "saturated" conditions by Lu *et al.*²⁰ Conversely, for $w/c = 0.33$ pastes of tricalcium silicate, Odler and Skalny²¹ have observed that the chemically bound water content per unit hydration (measured directly by X-ray diffraction) actually decreases with hydration time for sealed hydration either at 25° or 50°C . Thus, while past measurements have indicated that for $w/c = 0.3$ – 0.45 cement pastes, LOI-based degrees of hydration are in good agreement with both isothermal calorimetry and chemical shrinkage measurements,⁵ for $w/c = 0.25$ and lower cement pastes, particularly

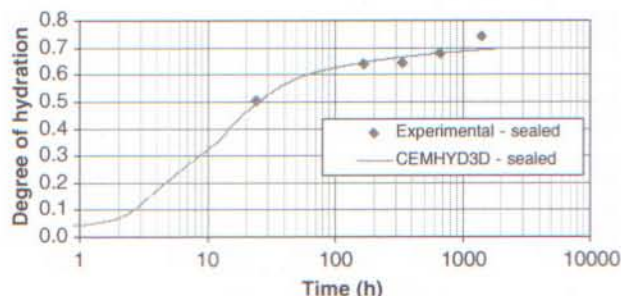


Fig. 5. Measured and CEMHYD3D predicted degree of hydration for $w/c = 0.35$ cement paste cured at 40°C under sealed conditions ($n = 3$).

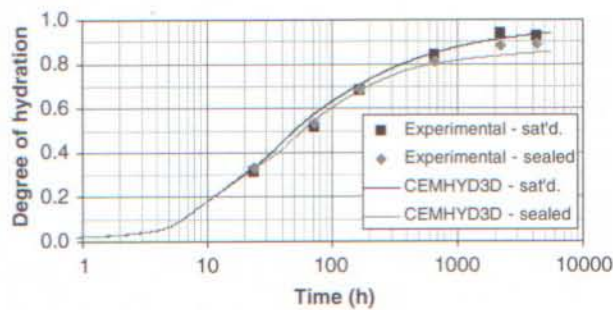


Fig. 6. Measured and CEMHYD3D predicted degrees of hydration for $w/c = 0.435$ cement pastes cured at 20°C .

when cured at higher temperatures, non-evaporable water content may no longer be a reliable measure of achieved hydration at later ages, as has already been noted for cement pastes with pozzolanic additions.^{22,23}

(2) LTC Scans

As many of the LTC scans have been presented elsewhere,^{7,24,25} here, only two representative series will be presented to introduce the subsequent analysis of percolated capillary porosity volume fraction. Figs. 10 and 11 show a series of LTC scans after various hydration times for a $w/c = 0.35$ cement paste cured under saturated and sealed conditions, respectively. As mentioned in the Section II, the specimens cured under sealed conditions were resaturated (typically for 1 day) before the LTC scans. As many as three distinct peaks are observed in an individual LTC scan, corresponding to percolated capillary pores with a freezing (peak) temperature of about -15°C , percolated open gel pores freezing at about -5°C , and percolated dense gel pores freezing between -40° and -45°C .⁶ As mentioned earlier, the water frozen at -25° and -40° to -45°C may also include water in depercolated capillary pores that are connected together by open gel pores or dense gel pores, respectively. In Fig. 10, as hydration progresses, the percolated capillary pores are observed to depercolate as the -15°C peak disappears between 3 and 4 days hydration, while the open gel pores depercolate later, with the -25°C peak disappearing between 14 and 30 days.

As shown in Fig. 11, a substantially different behavior is observed for the specimens cured under sealed conditions and resaturated before the LTC scan. While the capillary pores in these systems do initially depercolate, they actually repercolate at ages of 14 days and beyond. Under sealed curing conditions, as chemical shrinkage and self-desiccation occur, shrinkage stresses and strains will be imposed on the C-S-H gel and its local shrinkage within a basically non-shrinking 3-D framework could reopen the originally closed capillary pore entryways.⁷ In addition, microcracking could also contribute to the detected percolated capillary porosity in Fig. 11 at later ages. A similar repercolation of originally depercolated capillary pores has been observed by Bager and Sellevold¹⁴ for hydrated specimens exposed to drying, followed by resaturation. This repercolation of

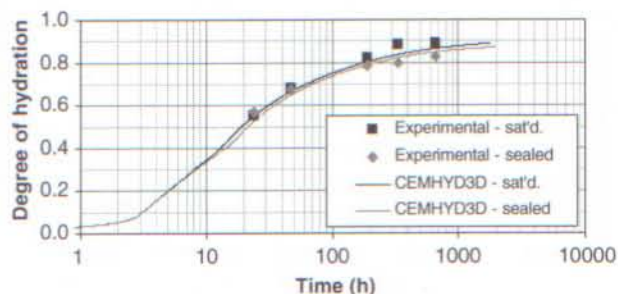


Fig. 7. Measured and CEMHYD3D predicted degrees of hydration for $w/c = 0.45$ cement pastes cured at 40°C .

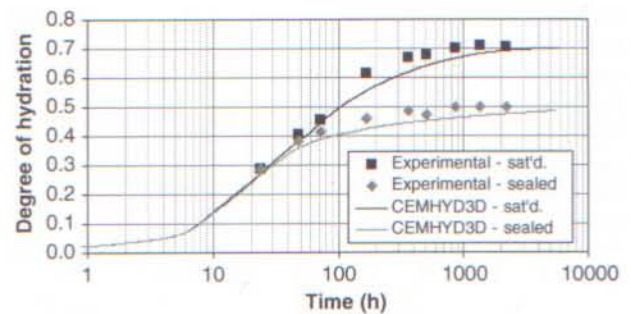


Fig. 8. Measured and CEMHYD3D predicted degrees of hydration for $w/c = 0.25$ cement pastes cured at 20°C .

a network of capillary (size) pores would be expected to have a large influence on transport properties (as indicated by the measurements of Powers *et al.*² mentioned previously) and durability in general. Particularly, the freeze-thaw performance of the specimens could be reduced as directly indicated by the higher freezable water contents for temperatures above -20°C for the 14–50 days specimens. This observation reinforces the importance of avoiding this repercolation process by maintaining saturated curing conditions in low w/c cement-based materials, a condition that may sometimes only be assured by internal curing.⁷

Similar LTC scans were obtained for the other w/c specimens and also for the 40°C curing.^{7,24} One item of interest was that for the $w/c = 0.35$ specimens cured at 40°C , even though hydration is accelerated (as indicated by comparing Figs. 3 and 4), it takes a longer period of curing time and a greater degree of hydration to achieve the initial depercolation of the capillary porosity, as indicated by the disappearance of the -15°C peak. In the 40°C cement paste, depercolation according to the LTC scans was observed to occur between 7 and 14 days, as compared with the 3–4 days observed above for the 20°C saturated curing. This observation is in agreement with the development of a coarser capillary pore structure when curing at higher temperatures, as mentioned above.^{17,18}

(3) Capillary Porosity Percolation—LTC and CEMHYD3D

For the specimens cured under saturated conditions, for those LTC scans that exhibited a discernible peak close to -15°C , the peak height (peak value–baseline value) was measured as a simple direct indication of the amount of (percolated) freezable water. This is equivalent to assuming a proportionality factor of unity to convert from the peak-height units of W/g to units of volume fraction of (percolated) freezable water. The direct measurement of peak height was used as opposed to more conventional but complex approaches such as computing the peak area convoluted with the heat of fusion of water as a function of temperature, because of the generally large uncertainties in the appropriate values to use in the latter approach.²⁶ This peak height value was then directly compared with the volume fraction of percolated pores (with a voxel resolution of $1\ \mu\text{m}$) as

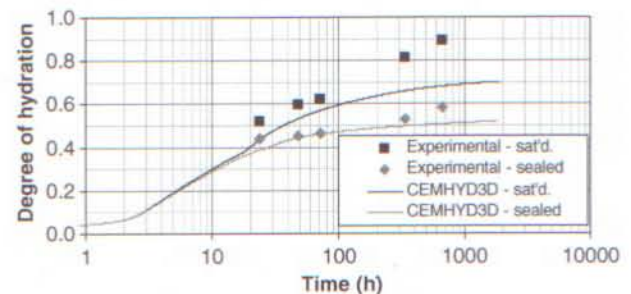


Fig. 9. Measured and CEMHYD3D predicted degrees of hydration for $w/c = 0.25$ cement pastes cured at 40°C .

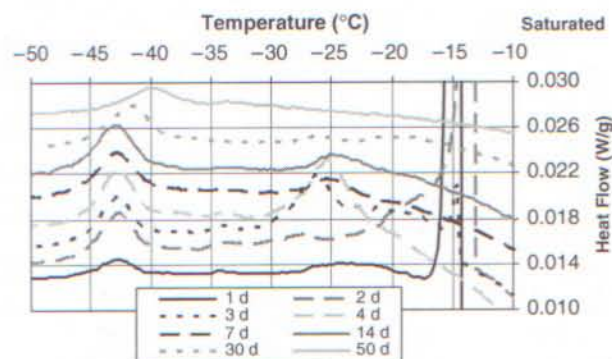


Fig. 10. Low-temperature calorimetry scans for a $w/c = 0.35$ ordinary portland cement paste cured under saturated conditions at 20°C for the ages indicated in the legend.

computed using a burning algorithm⁸ in the CEMHYD3D computer model. Because the LTC results are reported on a mass basis and CEMHYD3D provides a measure of the percolated capillary porosity volume fraction, a mass to volume basis conversion that also included the extra water that was imbibed into the saturated specimens because of chemical shrinkage was performed. Peak heights measured on replicate cement paste mixtures ($w/c = 0.35$, saturated curing at 20°C) exhibited a coefficient of variation of 15%.

Comparison plots are provided in Figs. 12–16 for the various w/c and curing temperatures used in this study. In Fig. 14, model results are presented for three separate executions of CEMHYD3D (with three different starting $w/c = 0.35$ microstructure representations) to provide some indication of model variability for the simulated percolated capillary porosity volume fraction. In general, reasonable agreement is observed between CEMHYD3D predictions and the values measured in the LTC scans, particularly for connected pore volume fractions above 0.15. Greater fluctuations would be expected at the lower connected pore volume fractions as the critical percolation/depercolation transition is approached,⁹ as indicated by the “noise” in the CEMHYD3D curves in Figs. 15 and 16, for example.

In Fig. 15, further justification for the modification of the local C–S–H distance (locations) from $n = 8$ –3 for the 40°C curing is observed. With the former fixed value of $n = 8$ voxels at all temperatures, the time (and degree of hydration) of the $w/c = 0.35$, 40°C depercolation would be vastly underpredicted, while the predictions with $n = 3$ are in better agreement with the experimental LTC measured peak heights.

Finally, the measured LTC peak heights were used in a similar manner to calculate the later age “damaged” (re)connected pore volume fractions for the specimens cured under sealed conditions. The damaged porosity was simply taken to be equivalent to the peak height of the peak close to -15°C in the LTC scans.

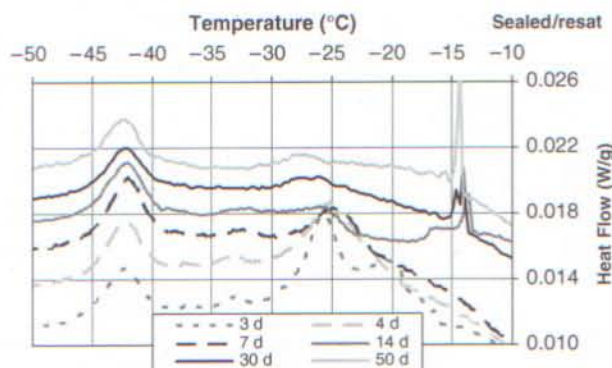


Fig. 11. Low-temperature calorimetry scans for a $w/c = 0.35$ ordinary portland cement paste cured under sealed conditions at 20°C for various ages indicated and then resaturated for 1 day.

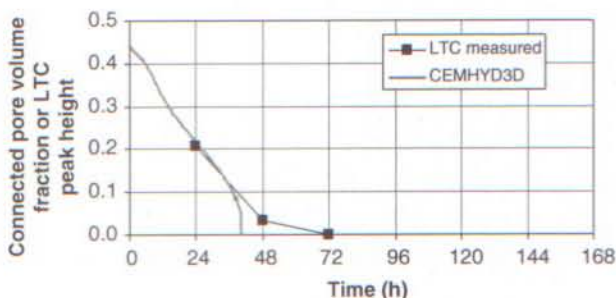


Fig. 12. Comparison of low-temperature calorimetry (LTC) estimated and CEMHYD3D predicted percolated capillary porosity volume fractions versus time for $w/c = 0.25$ cement paste hydrated under saturated conditions at 20°C.

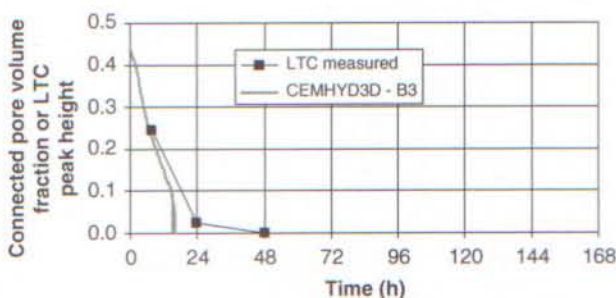


Fig. 13. Comparison of low-temperature calorimetry (LTC) estimated and CEMHYD3D predicted percolated capillary porosity volume fractions versus time for $w/c = 0.25$ cement paste hydrated under saturated conditions at 40°C.

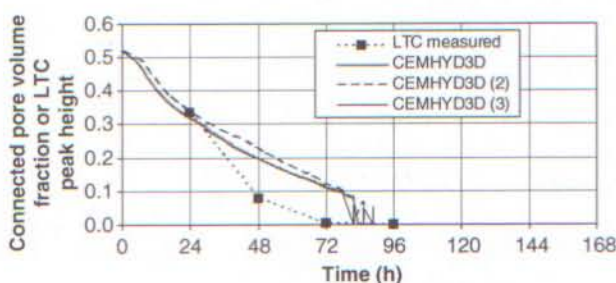


Fig. 14. Comparison of low-temperature calorimetry (LTC) estimated and CEMHYD3D predicted percolated capillary porosity volume fractions versus time for $w/c = 0.35$ cement paste hydrated under saturated conditions at 20°C. Model results for three different microstructures (created and hydrated with different random number seeds) are shown to provide some indication of model variability.

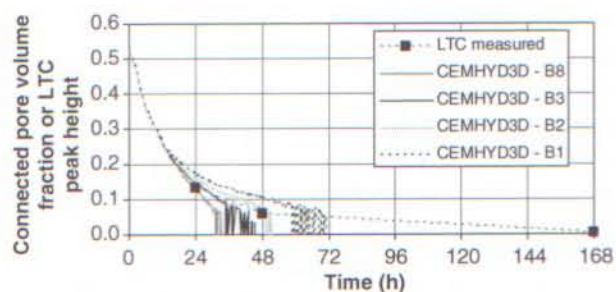


Fig. 15. Comparison of low-temperature calorimetry (LTC) estimated and CEMHYD3D predicted percolated capillary porosity volume fractions versus time for $w/c = 0.35$ cement paste hydrated under saturated conditions at 40°C.

The results, summarized in the graph in Fig. 17, indicate that damaged porosities of several percent volume fraction are possible and that the severity of the autogenous damage appears to increase with either a decrease in w/c or an increase in curing

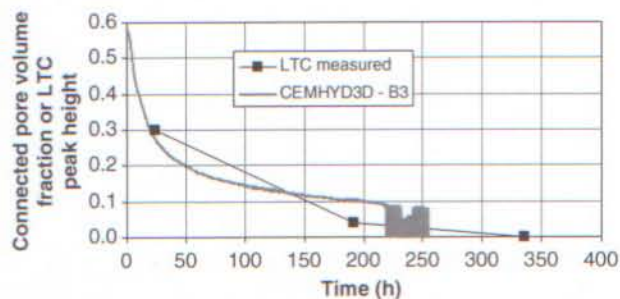


Fig. 16. Comparison of low-temperature calorimetry (LTC) estimated and CEMHYD3D predicted percolated capillary porosity volume fractions versus time for $w/c = 0.45$ cement paste hydrated under saturated conditions at 40°C .

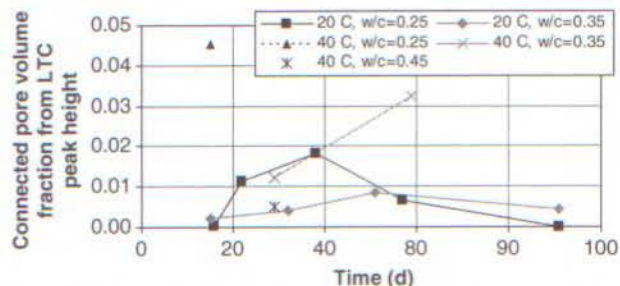


Fig. 17. Low-temperature calorimetry estimated percolated (damaged) capillary porosity volume fractions versus time for various cement pastes cured under sealed conditions.

temperature. This analysis is heavily dependent on the assumptions utilized to interpret the LTC data. Furthermore, it addresses only the change in connectivity of the capillary porosity because of self-desiccation (internal drying) and not the likely accompanying change in pore size. Both would be expected to contribute to an increase in the permeability of the cement paste, perhaps even on the order of the factor of 70 increase previously observed by Powers *et al.*²

V. Conclusions

The following points can be highlighted from this comparison of hydration and capillary porosity percolation as measured experimentally and predicted by CEMHYD3D:

- (1) In agreement with previous results,⁵ LOI measurements were found in this study to be a reliable indication of degree of hydration for $w/c \geq 0.35$ cement pastes, consistent with measured developments of compressive strength and heat of hydration. However, for $w/c = 0.25$ cement pastes and particularly for 40°C curing, the non-evaporable water content per unit hydration appears to increase with time.^{19,20} Under higher temperature curing conditions, LOI-interpreted degrees of hydration should not be used for cement pastes with $w/c \leq 0.25$.
- (2) Sealed curing can result in a repercolation of the capillary porosity that was initially depercolated by hydration, because of chemical shrinkage and its accompanying self-desiccation inducing autogenous stresses and strains on the cementitious gel-like hydrated microstructure.
- (3) While an increase in curing temperature from 20° to 40°C significantly accelerates cement hydration, it also produces a coarser capillary porosity system that takes longer to achieve complete depercolation in $w/c = 0.35$ cement pastes (both in terms of required time and degree of hydration).
- (4) In general, reasonable agreement was observed between the experimental measurements and CEMHYD3D predictions both for achieved degrees of hydration and for the volume fractions of connected capillary porosity.

(5) The volume fraction of connected capillary porosity created by autogenous damage under sealed curing could be effectively estimated, using the LTC measured peak height at -15°C , as was first "validated" for saturated curing conditions by comparison with the volumetric predictions of the CEMHYD3D model. Based on the limited experimental data obtained to date, the damage appears to increase with either a decrease in w/c or an increase in curing temperature.

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