

Ten Observations from Experiments to Quantify Water Movement and Porosity Percolation in Hydrating Cement Pastes

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TEN OBSERVATIONS FROM EXPERIMENTS TO QUANTIFY WATER MOVEMENT AND POROSITY PERCOLATION IN HYDRATING CEMENT PASTES

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ABSTRACT

The transport properties and durability performance of concrete structures are both strongly influenced by the three-dimensional microstructure that is established during early age placement and curing. This paper will present observations from two experimental techniques that have been applied to examining this early age microstructure development. First, x-ray absorption measurements are applied to study water (and cement particle) movement during settlement, drying, and curing. Five observations from a series of experiments conducted on single layer and bilayer composite specimens are presented and supported by experimental data. The influences of curing conditions, water-to-cement mass ratio (w/c), cement particle size distribution, shrinkage-reducing admixtures (SRAs), and internal curing via the addition of saturated lightweight aggregates (LWAs) are highlighted. Second, low temperature calorimetry (LTC) is utilized to examine the depercolation/repercolation of the capillary pores in a hydrating cement paste as a function of w/c, curing temperature, and the addition of various alkali ions or an SRA. Once again, five observations from this second type of experiment are presented and substantiated by experimental data. These ten observations have numerous implications for concrete curing practices, possible new applications for existing admixtures, and durability performance of field concrete.

INTRODUCTION

It is well known that the microstructure (particularly the pore structure) of concrete largely determines its transport properties and in many cases its ultimate service life. The pore structure is a dynamic system that changes dramatically during placement, curing and hydration, and field exposure and aging. Additionally, pores can be filled with water, vapor, or some combination of the two and the medium filling the pores will have a large influence on continuing hydration, transport, and common degradation reactions (carbonation for example). This paper focuses on two aspects of this developing pore structure, namely water movement within and through a cement paste microstructure during early age curing/drying and depercolation/repercolation of the capillary pores due to hydration and aging. The former process is investigated via the application of x-ray absorption measurements, while the latter is studied using low temperature calorimetry (LTC) experiments. Results are conveniently summarized as a set of ten critical observations of relevance both to basic research and to field applications.

EXPERIMENTAL METHODS

X-ray Absorption

The x-ray absorption technique and measurement procedures have been described in detail in a variety of publications.¹⁻⁵ The basic procedure is to expose the specimen of interest to a concentrated beam of x-rays and monitor the "quantity" of x-rays that are transmitted through the specimen. Previously, a point detector based on either a NaI or a Cd-Zn-Te (CZT) crystal has been employed,¹⁻⁵ but in the latest version of the commercially available equipment, a 256 x 256 camera detector with an active area of 25 mm x 25 mm is utilized. Specimens are placed in fixed locations between the x-ray source and the detector and sampled in both the spatial and temporal domains. Generally, the results are recorded as the number of counts received by the detector during a fixed integration time, normalized by the counts detected through a reference material specimen (such as water or dry cement powder) in the same integration time. In the graphs presented below, these count values are plotted against the spatial location within the specimen (thickness) for responses obtained at various curing times. More counts indicate a higher transmittance of the incoming x-rays and are generally interpreted as corresponding to a less dense material. For hydrating (and drying) cement paste, an increase in counts could indicate either a replacement of cement particles by water (during settling and bleeding for example) or a decrease in water content (after set is achieved) due to either drying or local rearrangement of water due to chemical shrinkage and self-desiccation. Previously, the relative standard uncertainty in the normalized counts has been determined to be on the order of 0.3%.²

Low Temperature Calorimetry

The low temperature calorimetry technique has also been described in several recent publications.⁶⁻⁸ A commercially available differential scanning calorimeter (DSC) with a cooling unit was utilized to cool small specimens of cement paste (mass typically between 30 mg to 90 mg) from 5 °C to -55 °C at a controlled rate of -0.5 °C/min. For temperatures between -100 °C and 500 °C, the DSC manufacturer has specified a constant calorimetric sensitivity of $\pm 2.5\%$, with a root-mean-square baseline noise of 1.5 μ W. Typical measured signals for a freezing scan are on the order of 0.5 mW to 1 mW. The peaks observed in a plot of heat flow versus temperature correspond to water freezing in pores with various size entryways (pore necks). The smaller the pore entryway, the more the freezing peak is depressed. Thus, a larger isolated water-filled pore will not freeze until the water in the smaller entryway pores surrounding it first freezes. The presence of, absence of, or change in these peaks can be used to infer critical information concerning the characteristic sizes of the "percolated" (connected) water-filled pores in the microstructure of the hydrating cement pastes. One advantage of LTC over mercury intrusion porosimetry and other techniques for assessing pore size and connectivity is that the specimens may be evaluated without any applied drying that might damage the pore structure.

OBSERVATIONS

1) Microstructural gradients established during settling/drying are different under sealed (saturated) and exposed (drying) conditions.

After casting, the microstructure of fresh cement paste can undergo significant changes due not only to settling (gravity) and bleeding, but also due to drying. For cement paste specimens 5 mm to 30 mm thick, the microstructural gradients developed through their thickness

depend strongly on their w/c and t curing, the initial settling may result the specimen, as indicated by the sn the width of the specimen in the bott particles descend and water "rises" specimens are naturally densified (fe due to these settlement processes, un of the specimens, it would be expec would exhibit a higher local w/c an Figure 2, much less microstructure n paste, as in a denser, more viscous nonexistent, and a basically flat x-ray

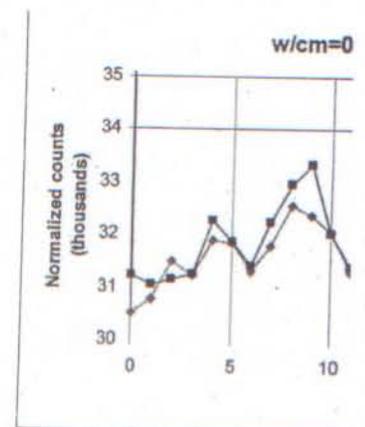


Figure 1. Normalized counts for x-rays cured under sealed conditions at 23 °C. Top of specimen is located at 30 mm.

When drying is superimposed forces may be imposed at the drying drying front begins its initial penetration will induce an extra densification microstructural gradient as a function preferential densification near the top on the differences between the 0.6 recommended practice of applying a curing first appears "dry" and free of surface formation of an equal or superior quality

cedures have been described in expose the specimen of interest to x-rays that are transmitted through NaI or a Cd-Zn-Te (CZT) crystal. Specially available equipment, a 256 x utilized. Specimens are placed in and sampled in both the spatial and number of counts received by the counts detected through a reference the same integration time. In the the spatial location within the ng times. More counts indicate a interpreted as corresponding to a aste, an increase in counts could (during settling and bleeding for red) due to either drying or local siccation. Previously, the relative ined to be on the order of 0.3 %.²

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can undergo significant changes e to drying. For cement paste eveloped through their thickness

depend strongly on their w/c and the exposure conditions. As shown in Figure 1, for sealed curing, the initial settling may result in a densification of the cement paste in the lower portion of the specimen, as indicated by the smaller number of x-rays (counts) that are transmitted through the width of the specimen in the bottom portion (31,000) vs. the top portion (34,000). As cement particles descend and water "rises" during settlement and bleeding, the lower portions of the specimens are naturally densified (fewer x-rays transmitted) more than the upper portions. Thus, due to these settlement processes, under sealed curing conditions or when water is ponded on top of the specimens, it would be expected that the upper portions of the specimens (surface layer) would exhibit a higher local w/c and ultimately a more porous microstructure. As illustrated in Figure 2, much less microstructure rearrangement of this type was observed in a w/c=0.3 cement paste, as in a denser, more viscous paste, settlement and its accompanying bleeding are nearly nonexistent, and a basically flat x-ray profile is observed.

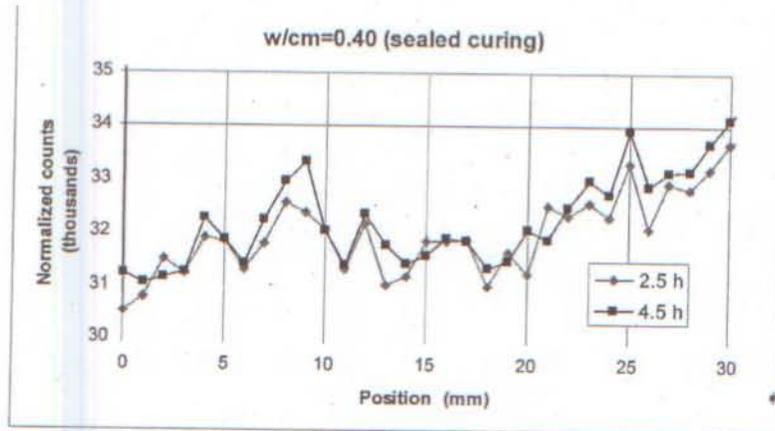


Figure 1. Normalized counts for x-rays transmitted through a w/cm=0.40 blended cement paste cured under sealed conditions at 23 °C, as a function of curing time (2.5 h or 4.5 h) and depth.⁴ Top of specimen is located at 30 mm.

When drying is superimposed on the settlement/bleeding process, additional capillary forces may be imposed at the drying surface, due to the menisci that are formed there as the drying front begins its initial penetration into the porous (set) microstructure.^{9,10} These forces will induce an extra densification at the top (exposed) surface, so that in this case, the microstructural gradient as a function of depth may remain relatively flat or may even exhibit a preferential densification near the top surface, as exemplified in Figure 3,¹ particularly focusing on the differences between the 0.67 h and the 4.67 h scans. From this perspective, the recommended practice of applying a curing compound only when the top surface of the concrete first appears "dry" and free of surface water¹¹ should also be beneficial in promoting the formation of an equal or superior quality surface layer in the concrete.

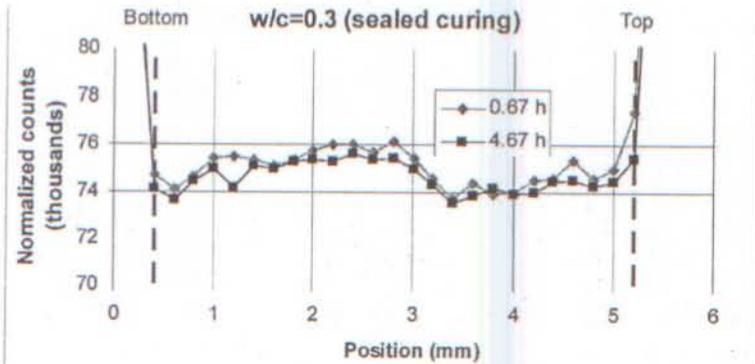


Figure 2. Normalized counts for x-rays transmitted through a $w/c=0.30$ cement paste cured under sealed conditions at $23\text{ }^{\circ}\text{C}$, as a function of curing time (0.67 h or 4.67 h) and depth.¹

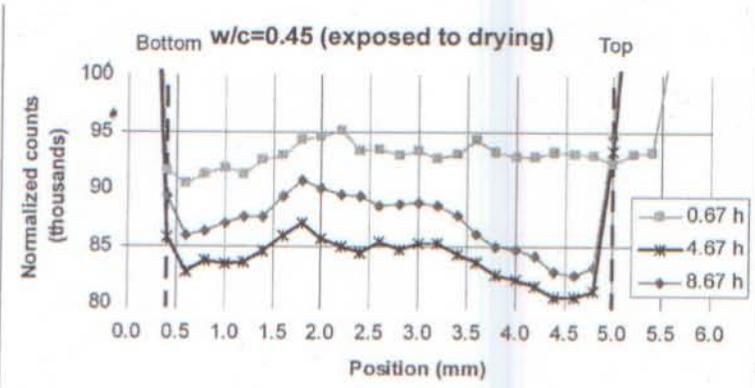


Figure 3. Normalized counts for x-rays transmitted through a $w/c=0.45$ portland cement paste immediately exposed to drying conditions ($23\text{ }^{\circ}\text{C}$ and 50 \% RH), as a function of curing time (0.67 h, 4.67 h or 8.67 h) and depth.¹ Top of specimen is located at about 5 mm.

2) After settling, 10 mm to 20 mm thick ordinary portland cement paste specimens without admixtures and with $w/c \leq 0.45$, dry out "uniformly" through their thickness.

Because the cement particles in a typical cement paste have a fairly wide particle size distribution (diameters ranging from submicron to about $100\text{ }\mu\text{m}$), the pore size distribution in the fresh paste (dispersion) also exhibits a wide range of pore sizes. Thus, unlike many materials which exhibit a sharp drying front that "intrudes" from the exposed surface inward, after settling, ordinary portland cement pastes with $w/c \leq 0.45$ dry out rather uniformly, as illustrated by the results shown in Figure 4. This "uniform" drying implies that the largest pores (some of which

could be part of bleed channels) thro when the specimen is exposed to a di those shown in Figure 4 were obtain was minimal.¹ Similar results have a specimen using magnetic resonance i curing of field concrete are critical, a concrete surface can actually be i hydrating cement paste at much i reinforcement.¹

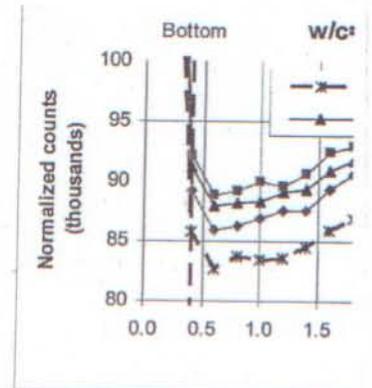
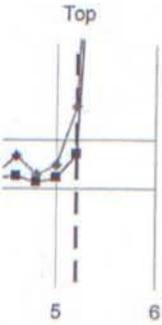


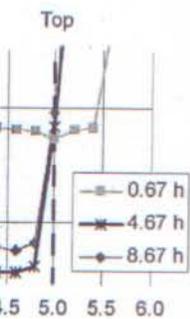
Figure 4. Normalized counts for x-rays transmitted through a $w/c=0.45$ portland cement paste immediately exposed to drying conditions ($23\text{ }^{\circ}\text{C}$ and 50 \% RH), as a function of curing time (4.67 h, 8.67 h, 12.67 h, or 24.67 h) and depth.¹ Top of specimen is located at about 0.5 mm.

3) In bilayer composite specimens, w structure to a finer one during either exposure, the finer layer will lose v structure layer on top of a coarser one under equivalent drying exposures.

During the initial experiments composite cement paste specimens we layers were w/c (for a fixed cement po of 0.45). In the former case, a higher its higher water volume fraction, wh coarser pore size distribution due to th As illustrated in Figures 5 and 6, rega always first moves preferentially from it is the finer one that is directly expo w/c cement paste layer over a higher the first 7 h while the exposed lower w a small amount of additional water t



h a $w/c=0.30$ cement paste cured (0.67 h or 4.67 h) and depth.¹



a $w/c=0.45$ portland cement paste (RH), as a function of curing time ed at about 5 mm.

cement paste specimens without their thickness. te have a fairly wide particle size (μm), the pore size distribution in sizes. Thus, unlike many materials osed surface inward, after settling, er uniformly, as illustrated by the the largest pores (some of which

could be part of bleed channels) throughout the thickness of the specimen are the first to empty when the specimen is exposed to a drying environment. It should be noted that results similar to those shown in Figure 4 were obtained for a $w/c=0.3$ cement paste where observable bleeding was minimal.¹ Similar results have also been obtained for a much thicker (50 mm) cement paste specimen using magnetic resonance imaging.¹² The potential implications of this observation for curing of field concrete are critical, as the drying that is observed to be occurring at the exposed concrete surface can actually be influencing the water content and microstructure of the hydrating cement paste at much greater depths, perhaps even at the depth of the steel reinforcement.¹

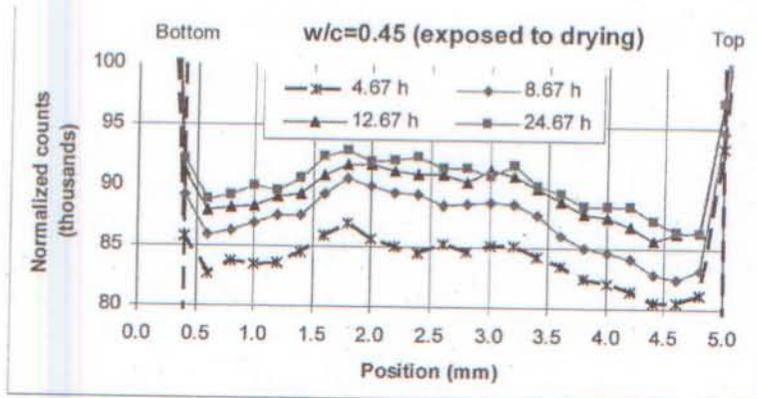


Figure 4. Normalized counts for x-rays transmitted through a $w/c=0.45$ portland cement paste immediately exposed to drying conditions (23 °C and 50 % RH), as a function of curing time (4.67 h, 8.67 h, 12.67 h, or 24.67 h) and depth.¹ Top of specimen is located at about 5 mm.

3) In bilayer composite specimens, water always first moves preferentially from a coarser pore structure to a finer one during either drying or sealed hydration. Eventually, during a drying exposure, the finer layer will lose water as well. A composite specimen with a finer pore structure layer on top of a coarser one will lose less water than one with the two layers reversed, under equivalent drying exposures.

During the initial experiments using the x-ray absorption technique, a variety of bilayer composite cement paste specimens were prepared.^{1,2} The two parameters varied between the two layers were w/c (for a fixed cement powder) and cement particle size distribution (for a fixed w/c of 0.45). In the former case, a higher w/c paste will have a coarser pore size distribution due to its higher water volume fraction, while in the latter case, the coarser cement will produce a coarser pore size distribution due to the increased spacing between the (fewer) cement particles. As illustrated in Figures 5 and 6, regardless of how the coarser pore structure is produced, water always first moves preferentially from the coarse pore structure layer to the finer one, even when it is the finer one that is directly exposed to the drying environment. In Figure 5, with a lower w/c cement paste layer over a higher w/c one, the higher w/c layer is seen to lose water during the first 7 h while the exposed lower w/c layer on top remains basically saturated, even imbibing a small amount of additional water to offset that "consumed" by chemical shrinkage during

hydration. For 11 h and beyond, further water loss from the higher w/c layer is minimal and the lower w/c layer also begins to dry out. In Figure 6, with a cement paste layer produced using a finer cement ($654 \text{ m}^2/\text{kg}$) over one produced using a coarser cement ($254 \text{ m}^2/\text{kg}$), the coarser layer is seen to lose water during the first 5 h while the finer layer remains saturated. For 7 h and beyond, further water loss from the coarser layer is minimal and the finer layer also begins to dry out. In both Figure 5 and Figure 6, each of the 4 mm to 5 mm thick cement paste layers is observed to dry out in a relatively uniform fashion throughout their thickness once drying begins, in agreement with observation # 2. It should be further noted that the initial (1 h or 3 h) microstructural gradients established through the thicknesses of the various layers are consistent with observation # 1 above.

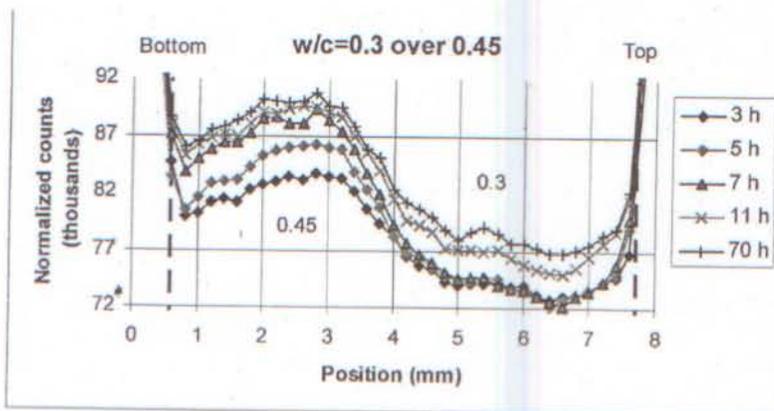


Figure 5. Normalized counts for x-rays transmitted through a w/c=0.3 over a w/c=0.45 bilayer portland cement paste immediately exposed to drying conditions (23°C and $50\% \text{ RH}$), as a function of curing time (3 h to 70 h) and depth.¹ Top of specimen is located at about 7.5 mm and the lower w/c cement paste layer is directly exposed to the drying environment.

This preferential water movement from a coarser pore structure to a finer one has implications both for curing and for the application of repair materials. In the former case, controlled permeability formwork¹³ and internal curing¹⁴ are two examples of how these principles can be used to advantage. In the latter case, the saturation level of the material being repaired and the pore structure of the repair material must be carefully coordinated to avoid significant water movement from the repair material to the in place material, while perhaps promoting some water movement from the in place material to the repair material to enhance its hydration and offset any water loss to the external environment.

4) Shrinkage-reducing admixtures (SRAs) significantly modify the drying profile of exposed cement paste specimens and reduce their drying rates. In a bilayer composite, water is preferentially first drawn from a layer with SRA into a layer without SRA.

Because SRAs significantly reduce the surface tension of the cement paste pore solution, they can have a large impact on both the drying rate and the shape of the drying profile.^{3,9,10} As illustrated in Figure 7, when a 2% SRA addition by mass of cement is made to a w/c=0.35

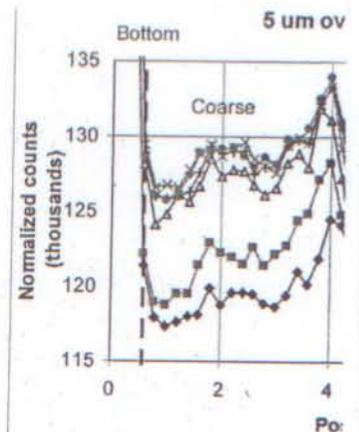


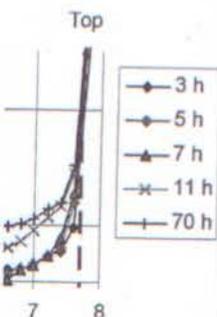
Figure 6. Normalized counts for x-ray paste immediately exposed to drying time (1 h to 19 h) and depth.² Top of paste layer is directly exposed to the d

rying environment. In contrast to the "flat" profile observed for about the first 6 h of drying, the coarser layer shows a sharp(er) drying front. It has been proposed³ that the presence of SRAs concentrates the SRA present in the tension of the pore solution in the top layer, which slows the drying process. This "capillary regime" of drying, while a "evaporative regime".^{3,9,10,15} Two principles are indicated, namely the usage of SRAs in a curing solution containing 10% SRA to enhance hydration.⁹

5) During hydration, in systems with surrounding hydrating cement paste

Previously, the x-ray absorptivity of water movement from a saturated ligament paste during early age curing.⁵ The air transmittance correlated linearly with measured in a separate experiment. microstructure development software.⁵

higher w/c layer is minimal and the cement paste layer produced using a finer cement (254 m²/kg), the coarser layer remains saturated. For 7 h and the finer layer also begins to dry and the 5 mm thick cement paste layers is at their thickness once drying begins, noted that the initial (1 h or 3 h) of the various layers are consistent



a w/c=0.3 over a w/c=0.45 bilayer cement paste immediately exposed to drying conditions (23 °C and 50 % RH), as a drying front is located at about 7.5 mm and the finer cement paste layer is directly exposed to the drying environment.

the pore structure to a finer one has been observed in repair materials. In the former case, the repair materials are two examples of how these materials behave at different curing duration level of the material being repaired. The curing process should be carefully coordinated to avoid the repair material, while perhaps the repair material to enhance its performance.

To quantify the drying profile of exposed repair materials in a bilayer composite, water is measured in the repair material without SRA.

The effect of the cement paste pore solution, the shape of the drying profile.^{3,9,10} As the repair material is made to a w/c=0.35

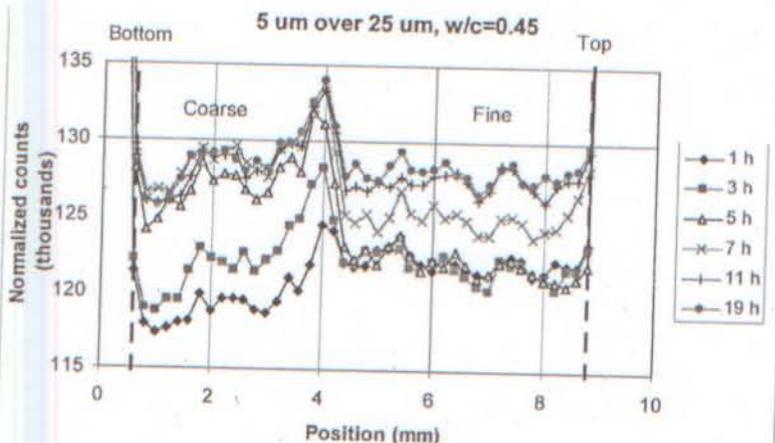


Figure 6. Normalized counts for x-rays transmitted through a w/c=0.45 bilayer portland cement paste immediately exposed to drying conditions (23 °C and 50 % RH), as a function of curing time (1 h to 19 h) and depth.² Top of specimen is located at about 9 mm and the finer cement paste layer is directly exposed to the drying environment.

cement paste, a sharp(er) drying front is formed intruding downward from the exposed surface, in contrast to the “flat” profile observed in Figure 4, for example. The drying front maintains its form for about the first 6 h of drying, followed by more uniform drying throughout the specimen thickness. It has been proposed³ that the initial water removal from the exposed surface concentrates the SRA present in that top layer. As this concurrently decreases the surface tension of the pore solution in the top layer, that layer is unable to draw the higher surface tension pore solution up from deeper within the specimen. Hence, the initial penetration of the drying front into the specimen is observed. This initial penetration of the drying front also substantially slows the drying process as the porous material containing the SRA enters its “capillary regime” of drying, while a material without the SRA remains in its higher drying rate “evaporative regime”.^{3,9,10,15} Two practical implications of this observation have recently been indicated, namely the usage of SRAs to reduce plastic shrinkage cracking¹⁰ and the application of a curing solution containing 10 % to 20 % SRA to reduce evaporative water loss and thus enhance hydration.⁹

5) During hydration, in systems with internal curing, water movement from water reservoirs to the surrounding hydrating cement paste can be detected using x-ray absorption measurements.

Previously, the x-ray absorption system with a point detector has been utilized to monitor water movement from a saturated lightweight aggregate (LWA) to adjacent hydrating cement paste during early age curing.⁵ The amount of water movement indicated by the change in x-ray transmittance correlated linearly with the chemical shrinkage of the hydrating cement paste, as measured in a separate experiment or as modeled using the CEMHYD3D hydration and microstructure development software.⁵ More recently, similar x-ray transmittance data have

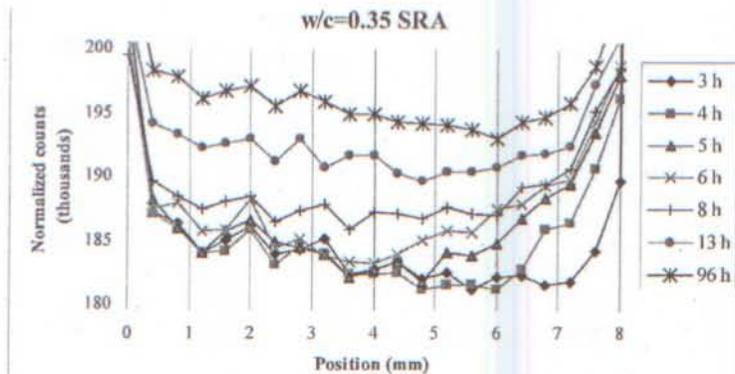


Figure 7. Normalized counts for x-rays transmitted through a $w/c=0.35$ portland cement paste with a 2 % SRA addition by mass of cement, immediately exposed to drying conditions (23 °C and 50 % RH), as a function of curing time (3 h to 96 h) and depth.³ Top of specimen is located at about 8 mm.

been obtained utilizing the new camera detector that provides a complete 256 x 256 pixel image of the materials being investigated, with a resolution of 0.1 mm/pixel. A single ≈ 10 mm saturated LWA particle was surrounded by a $w/c=0.3$ cement paste and placed in a thin sealed plastic container (width of about 8 mm). A rubber gasket was used as an exterior guard ring surrounding the cement paste/LWA specimen. The container was placed between the x-ray source and the camera detector and x-ray images were acquired after various hydration times, as illustrated in Figure 8. The images obtained by subtracting the image at 0.5 h from those obtained after different hydration times clearly indicate the preferential movement of water out of the saturated LWA into the surrounding cement paste to satisfy the water demand in the cement paste, created by the chemical shrinkage that is accompanying the ongoing hydration. In the future, it is planned to conduct three-dimensional x-ray microtomography experiments at a higher spatial resolution on mortars with internal curing, to hopefully observe this same process in 3-D.

6) In low w/c cement pastes hydrated under sealed conditions, capillary porosity first depercolates, but later repercolates due to self-desiccation stresses and C-S-H rearrangement (and possibly microcracking).

Typical LTC scans for a $w/c=0.35$ cement paste hydrated at 20 °C under saturated conditions are provided in Figure 9. Three peaks are commonly observed in the LTC scans: one near -15 °C corresponding to water in percolated capillary pores, one at about -25 °C corresponding to open gel pores (entryways), and one between -40 °C and -45 °C, corresponding to dense gel pores, using the naming convention proposed by Snyder and Bentz.⁶ The scans in Figure 9 follow a typical evolution as the capillary pores become depercolated somewhere between 3 d and 4 d, followed by a later depercolation of open gel pores between 14 d and 30 d. Beyond this time, the only peak observed in the LTC scans corresponds to those pores that are percolated via entryways composed of the dense gel pores, and the height of this peak is

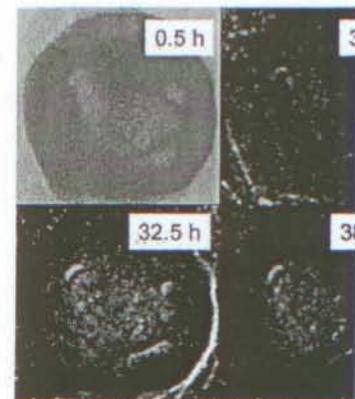
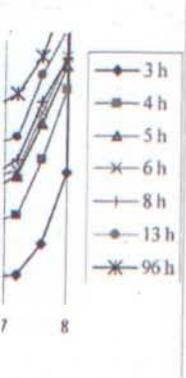


Figure 8. X-ray images for internal single initially saturated LWA particle brighter (less dense) saturated LWA particle by a rubber gasket. Subsequent images obtained after various hydration time while darker areas indicate wetting. At the right specimen edge indicates the x-ray source and camera detector

continually decreasing along with the. The height of the capillary pore peak connected (percolated) fraction of cap

Even more interesting results presents a series of LTC scans for w resaturated for a single day prior to tl by Bager and Sellevold concerning th observed that during sealed curing, v (14 d and beyond) repercolate due t autogenous strain development, cree observed in very low $w/c=0.25$ ceme the initial depercolation of the capilla needed to maintain saturated conditi As observed in Figure 10, the meas correlation developed via the CEMH be conveniently converted to a damag

7) This repercolation has also been under saturated curing conditions. A "stabilize" the C-S-H so that this repe It has been observed that th influence on porosity depercolation/re



with a $w/c=0.35$ portland cement paste exposed to drying conditions (23°C depth.³ Top of specimen is located

is a complete 256×256 pixel image 0.1 mm/pixel . A single $\approx 10 \text{ mm}$ of paste and placed in a thin sealed was used as an exterior guard ring ner was placed between the x-ray ed after various hydration times, as ng the image at 0.5 h from those preferential movement of water out o satisfy the water demand in the npanying the ongoing hydration. In micromotography experiments at a eepfully observe this same process

conditions, capillary porosity first stresses and C-S-H rearrangement ydrated at 20°C under saturated ly observed in the LTC scans: one ary pores, one at about -25°C n -40°C and -45°C , corresponding Snyder and Bentz.⁶ The scans in become depercolated somewhere n gel pores between 14 d and 30 d. corresponds to those pores that are l the height of this peak is

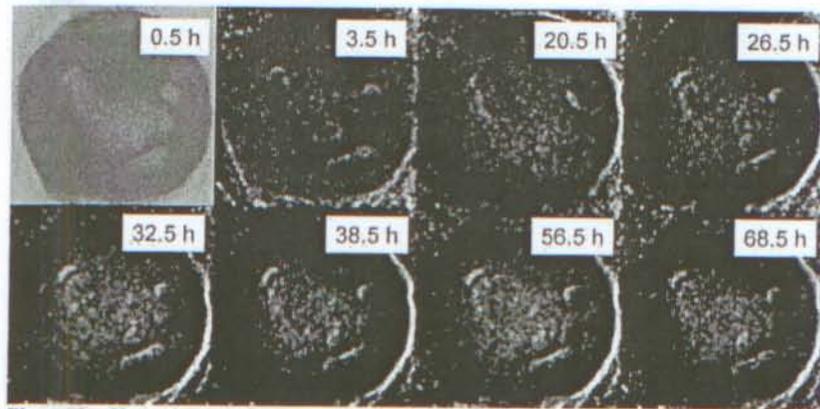


Figure 8. X-ray images for internal curing of $w/c=0.3$ hydrating cement paste surrounding a single initially saturated LWA particle. Top left image is initial x-ray view of system with brighter (less dense) saturated LWA particle as central portion of circular specimen, surrounded by a rubber gasket. Subsequent images are subtractions of this initial image from images obtained after various hydration times. In the subtracted images, brighter areas indicate drying while darker areas indicate wetting. Hydration times are as indicated. The slight halo observed at the right specimen edge indicates a small misalignment of the specimen during movement of the x-ray source and camera detector between consecutive images.

continually decreasing along with the total porosity of the specimen due to continuing hydration. The height of the capillary pore peak near -15°C has recently been successfully correlated to the connected (percolated) fraction of capillary porosity as predicted by the CEMHYD3D model.¹⁶

Even more interesting results are obtained when sealed curing is considered. Figure 10 presents a series of LTC scans for $w/c=0.35$ specimens cured under sealed conditions and then resaturated for a single day prior to the LTC scan. Similar to the observations made previously by Bager and Sellevold concerning the influence of drying/resaturation on the LTC scans,¹⁷ it is observed that during sealed curing, while the capillary pores do initially depercolate, they later (14 d and beyond) re-percolate due to an "aging" process that likely includes self-desiccation, autogenous strain development, creep, and possibly microcracking. This re-percolation is even observed in very low $w/c=0.25$ cement pastes cured under supposedly "saturated" conditions, as the initial depercolation of the capillary porosity reduces the rate of water imbibition below that needed to maintain saturated conditions within these small (2 mm to 5 mm thick) specimens.¹⁶ As observed in Figure 10, the measured "damage" becomes more severe with age; using the correlation developed via the CEMHYD3D model, the observed peak heights in Figure 10 can be conveniently converted to a damaged or re-percolated pore volume fraction.¹⁶

7) This re-percolation has also been observed in a low alkali $w/c=0.40$ cement paste hydrated under saturated curing conditions. Alkali additions, particularly lithium, to this paste appear to "stabilize" the C-S-H so that this re-percolation was not observed.

It has been observed that the alkali level of the portland cement also has a strong influence on porosity depercolation/repercolation, likely via its influence on the morphology and

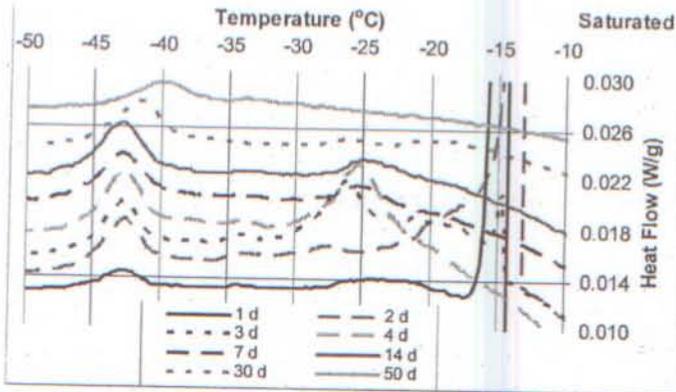


Figure 9. LTC scans for a $w/c=0.35$ ordinary portland cement paste cured under saturated conditions at $20\text{ }^{\circ}\text{C}$ for various ages.

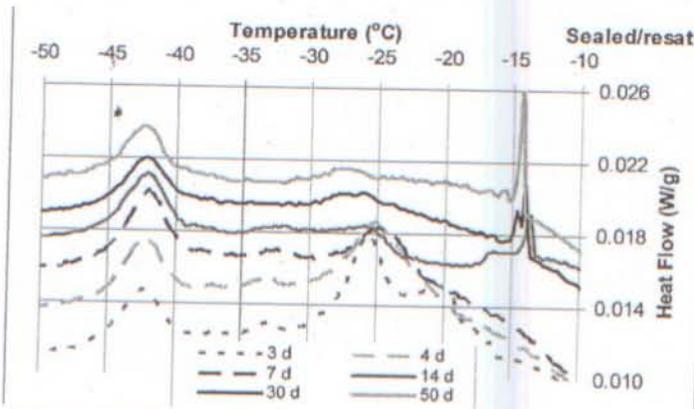


Figure 10. LTC scans for a $w/c=0.35$ ordinary portland cement paste cured under sealed conditions at $20\text{ }^{\circ}\text{C}$ for various ages and then resaturated for one day.

crystallinity of the calcium silicate hydrate (C-S-H) gel that is the dominant reaction product of portland cement hydration. For example, as shown in Figure 11, for a low alkali $w/c=0.4$ cement paste (0.093 % Na_2O and 0.186 % K_2O per unit mass of cement), saturated curing for an extended period of time (over 100 d) results in the (re)formation of a highly percolated capillary pore structure in a system where the capillary porosity had initially depercolated due to hydration.⁸ For a $w/c=0.4$ cement paste, it is unlikely that the observed repercolation is due to the "self-desiccation" aging described above. Instead, it appears that the C-S-H in the low alkali cement paste is more freely able to undergo rearrangement (some combination of shrinkage and creep) even in a saturated environment. As illustrated in Figure 11, the addition of extra alkali

ions seems to stabilize the C-S-H structure. Researchers have indicated that the crystalline (stable) C-S-H with a specific morphology.^{18,19} According to recent research, like C-S-H microstructures would be connected capillary pore structure that

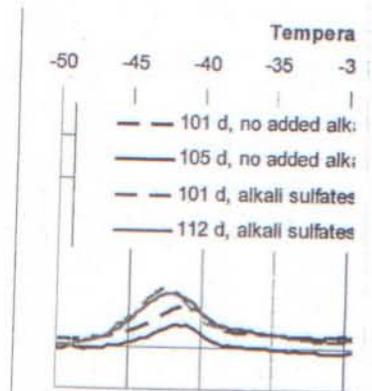
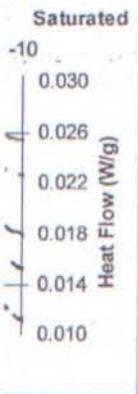


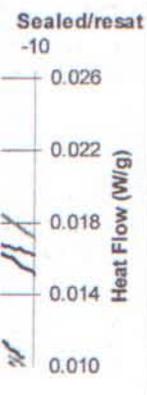
Figure 11. LTC scans for a $w/c=0.4$ cement paste cured at $20\text{ }^{\circ}\text{C}$, with and without added alkali.

8) While hydration is indeed accelerated (and hydration) for the capillary pore structure at high temperature curing.

It is well known that an increase in curing temperature generally produces a higher degree of hydration. Surprisingly, that as shown in Figure 12, the degree of hydration in a $w/c=0.35$ cement paste is as opposed to between 3 d and 4 d of curing. At the higher curing temperature and in terms of the necessary degree of hydration, the internal relative humidity measured by Persson,²³ and would be expected to be higher at higher temperatures. The CEMHYD3D model incorporates this effect by having the degree of hydration increase with temperature and good agreement has been shown with experimental data.¹⁶ As with $20\text{ }^{\circ}\text{C}$ curing, the data exhibit (re)percolated capillary pore structure



cement paste cured under saturated



d cement paste cured under sealed one day.

is the dominant reaction product of Figure 11, for a low alkali w/c=0.4 cement (of cement), saturated curing for an duration of a highly percolated capillary had initially depercolated due to the observed repercolation is due to reasons that the C-S-H in the low alkali (some combination of shrinkage and Figure 11, the addition of extra alkali

ions seems to stabilize the C-S-H so that this repercolation is largely not observed.⁶ Several researchers have indicated that the presence of increased alkalis tends to produce a more crystalline (stable) C-S-H with a greater propensity towards a plate (lath)-like structural morphology.^{18,19} According to recent three-dimensional microstructure-based simulations, plate-like C-S-H microstructures would be expected to be more efficient at depercolating an originally connected capillary pore structure than ones based on a totally random morphology.²⁰

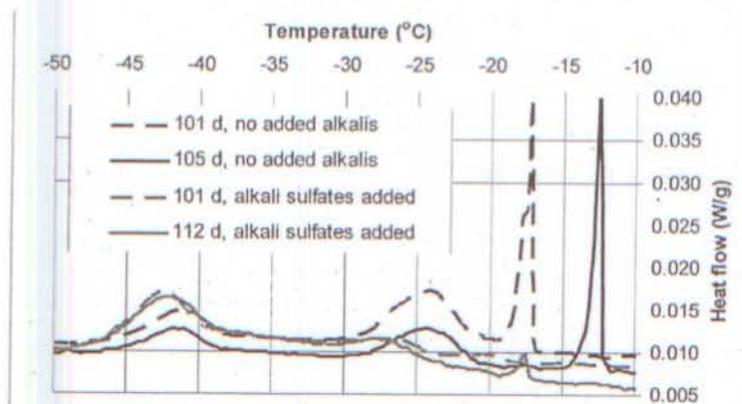
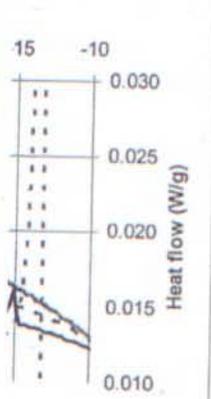


Figure 11. LTC scans for a w/c=0.40 low alkali portland cement paste cured under saturated conditions at 20 °C, with and without the addition of alkali sulfates.^{7,8}

8) While hydration is indeed accelerated at higher temperatures (e.g., 40 °C), it takes more time (and hydration) for the capillary pores to depercolate, implying a “coarser” pore structure for high temperature curing.

It is well known that an increase in temperature accelerates hydration rates in cement-based materials and generally produces a coarser pore structure.^{21,22} Thus, it may come as no surprise, that as shown in Figure 12, for hydration at 40 °C, the depercolation of the capillary porosity in a w/c=0.35 cement paste is delayed to occur between 7 d and 14 d of saturated curing, as opposed to between 3 d and 4 d observed for the 20 °C curing of a similar paste shown in Figure 9. At the higher curing temperature, the depercolation thus takes longer both in terms of time and in terms of the necessary degree of hydration. This observation would be consistent with the internal relative humidity measurements as a function of curing temperature recently presented by Persson,²³ and would suggest the formation of a denser C-S-H gel at higher temperatures. The CEMHYD3D version 3.0 computer model²⁴ has recently been modified to incorporate this effect by having the local C-S-H precipitation be a function of curing temperature and good agreement has been observed between the revised model and the experimental data.¹⁶ As with 20 °C curing, sealed/resaturated w/c=0.35 cement pastes also exhibit (re)percolated capillary pore structures after 28 d or more of sealed curing at 40 °C.



ement paste cured under saturated

percolation of the capillary porosity

ing saturated conditions in concrete Swayze²⁵ and Powers²⁶ separately regimen, the former to offset the ures, and the latter to promote frost r an intermediate range of w/c ratios d by ponding of water on top of the ore structure after 14 d total curing d throughout the 14 d. For this llowed by saturation appears to be l sealed curing is more effective at hydration in the smaller pores and ue to chemical shrinkage and self-

sion of the pore solution, it can also : temperatures, so that significantly curing ages of up to several weeks. r (and pore solution) by as much as resses in any partially water-filled ng point depression in a given size : controversy exists as to whether it l surface tension.²⁷ If one were to s have already been measured in the experimental results of Powers and ce tension due to the addition of an

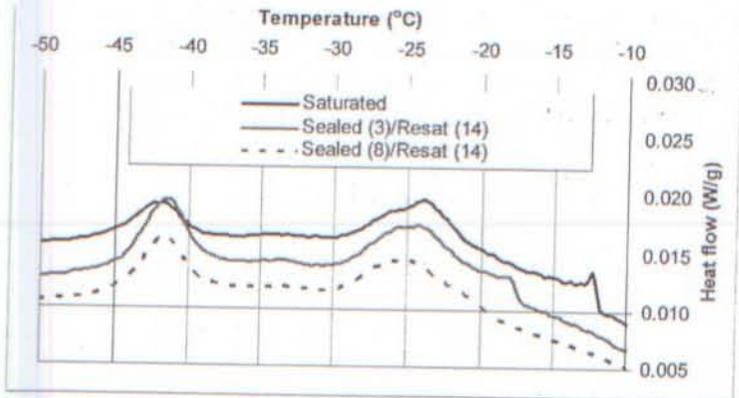


Figure 13. LTC scans for a w/c=0.45 ordinary portland cement paste cured under "sealed/saturated" conditions at 40 °C for 14 d of total curing time.

SRA, one would expect freezing point depressions of -45 °C and -25 °C to be shifted to values of about -19 °C and -12 °C, respectively. Thus, these peaks would be occurring in the same temperature range near -15 °C where freezing in the percolated capillary pores is usually observed at the scanning rates of -0.5 °C/min typically employed in these LTC experiments.

As shown by the results presented in Figure 14, this indeed seems to be the case²⁸ for a w/c=0.35 cement paste with a 3 % SRA addition by mass of cement cured at 20 °C under saturated conditions. At ages up to 14 d, the only peaks observed in the LTC scans are in the temperature range of about -12 °C to about -20 °C, and in some cases, two separate peaks are observed for a given specimen within this temperature range. It is only at later ages that measurable peaks appear near -25 °C (14 d and 21 d) and -45 °C (21 d) for the open and dense gel pores usually detected under saturated curing (after 1 d to 2 d in Figure 9). This could suggest that this particular SRA is being effectively removed from the "free" pore solution (specifically in the smaller pore entryways) after 21 d of hydration at 20 °C. Further support for these hypotheses can be found in Figure 15, where the LTC scans for specimens cured between 14 d and 21 d under various combinations of saturated and sealed/resaturated curing are presented. A shift of the LTC peaks to lower temperatures, that would be consistent with a removal of the SRA from the pore solution in the smaller pore entryways during hydration, is clearly indicated. While the experimental results in Figures 14 and 15 are consistent with the hypotheses made above, at least two other possibilities must be recognized: the SRA could modify (coarsen) the nanostructure of the C-S-H gel such that the entryway pores sizes (formed during early age hydration) are increased substantially or it could modify the solid-liquid surface tension in the same proportion as it modifies the liquid-gas surface tension. Further experiments are underway to clarify the influence of SRA on freezable water content,²⁸ but the undeniable fact that can be taken from comparing Figure 14 to Figure 9 is that whatever the reason, at ages up to 14 d the cement paste prepared with the 3 % SRA addition has substantially more freezable water at temperatures in the range from -10 °C to -20 °C than the control specimen prepared without SRA. Since SRAs also sometimes function as air detrainers²⁹ in the fresh concrete

mixture, their possible detrimental influence on early age frost resistance may be a topic worthy of further consideration.

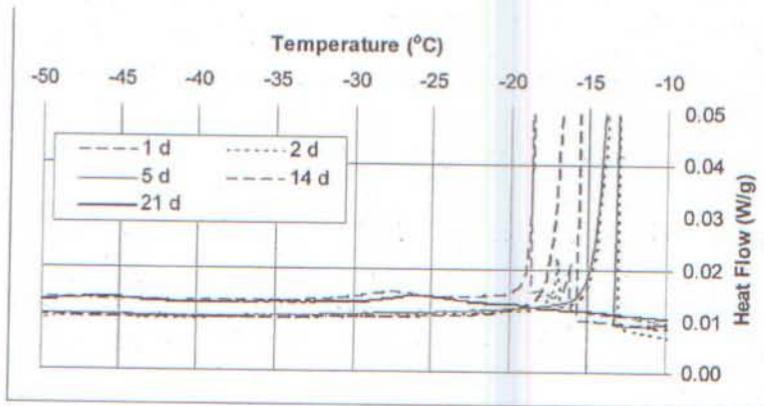


Figure 14. LTC scans for a $w/c=0.35$ ordinary portland cement paste with a 3 % SRA addition by mass of cement, cured under saturated conditions at 20 °C for various ages.²⁸

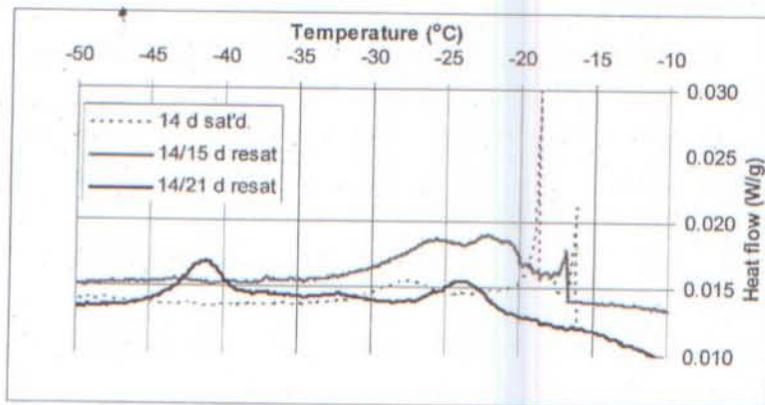


Figure 15. LTC scans for a $w/c=0.35$ ordinary portland cement paste with a 3 % SRA addition by mass of cement, cured at 20 °C with either 14 d of saturated curing or 14 d of sealed curing, followed by resaturation and further curing for either 1 d or 7 d.

CONCLUSIONS

X-ray absorption and low temperature calorimetry are valuable tools for studying curing and hydration of cement paste, the former for examining water movement during initial placement and curing, and the latter for quantifying the percolation state of the capillary porosity during hydration and aging. Many of the ten observations presented in this paper would not have

been predicted a priori, so both technical field of cement-based materials and scientific implications of the observations were and durability of cement-based materials

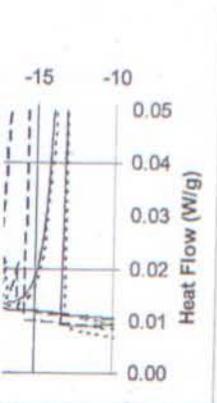
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The author would like to acknowledge the Technical University of Denmark and BFRL/NIST for their thorough review

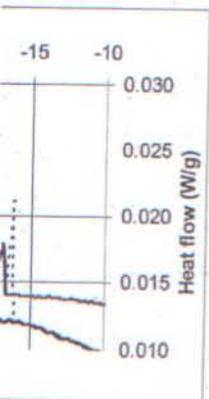
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ost resistance may be a topic worthy



ent paste with a 3 % SRA addition for various ages.²⁸



ent paste with a 3 % SRA addition under sealed curing or 14 d of sealed curing, d.

valuable tools for studying curing g water movement during initial ation state of the capillary porosity ented in this paper would not have

been predicted a priori, so both techniques are clearly advancing the state of knowledge in the field of cement-based materials science research. In addition, numerous practical (field) implications of the observations were provided in the contexts of curing, transport properties, and durability of cement-based materials.

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ALKALI SILICA REACTIVITY OF

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ABSTRACT

Silica fume is widely known. There has been recent concern, how present in sources that have been aggregates in high alkali environment explores silica fume with various aggregate for ASR. It was observed that silica fume but that keeping the maximum aggregate expansion due to ASR in the silica fume

INTRODUCTION

Alkali-silica reaction (ASR) is when three factors are present: 1) alkali reactive siliceous aggregates, and 3) moisture. These aggregates and cause the formation of expansive products causing cracking in the concrete. It has been observed that these reactive siliceous aggregates, that act as reactive siliceous aggregates, that these agglomerates have been observed in inadequate mixing procedures.^{2,3} The however. Some studies have shown that that agglomerates decrease expansion; however, these have been summarized by the authors previously.

The study described in this paper is a review of the literature with regard to this subject. It will discuss differences in testing regimes, differences