Influence of alkalis on porosity percolation in hydrating cement pastes

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Abstract

Loss-on-ignition (LOI) measurements and low temperature calorimetry (LTC) are used to study the properties of hydrating cement pastes with various quantities of alkalis. In addition to the well-known acceleration of early age hydration and "retardation" of later age hydration, the alkalis are observed to have a significant effect on the percolation of the porosity in the hydrating systems, as assessed using the LTC technique. At equivalent degrees of hydration, the capillary pores in cement pastes with sufficient added alkalis may depercolate while those in lower alkali cement pastes remain percolated. A simple dissolution/precipitation three-dimensional microstructural model is applied to examine the potential effects of hydration product morphology (random, needles, and plates or laths) on pore space percolation. The model suggests that the observed experimental results could be consistent with the higher alkali levels modifying the morphology of the C–S–H gel to produce more lath-like hydration products, as has been observed by others previously using electron microscopy. Potential implications for the transport properties and durability of these materials are discussed.
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1. Introduction

The alkali content of cements has long been a subject of interest, due both to the role of alkalis in deleterious alkali-silica reactions (ASR) and also to their influence on the hydration and microstructure of cement paste. It is generally accepted that potassium and sodium ions (present along with either sulfates or hydroxides) accelerate the early hydration of cement, while resulting in reduced hydration and strength at later ages [1,2]. Electron microscopy observations have suggested that the alkalis also modify the morphology of the calcium silicate hydrate gel (C–S–H) formed during hydration, leading to the formation of plate (lath)-like gel hydration products [3,4]. The influences of alkalis and the altered morphology of the C–S–H gel on transport properties and durability have been studied much less. Recently [5], low temperature calorimetry (LTC) results have indicated that after about 100 d of saturated curing, cement pastes with a water-to-cement ratio (w/c) of 0.40 by mass fraction, containing significant additional alkalis, exhibited a depercolated (disconnected) capillary pore structure, while the capillary pores in the original (low alkali) cement paste were still highly percolated. This paper presents further studies that have been conducted to verify this observation, using a combination of LTC and loss-on-ignition (LOI) experimental techniques.

2. Experimental

Cement pastes with a w/c of 0.40 were prepared by mixing cement and concrete reference laboratory (CCRL) proficiency cement sample 140 [6] with water at 20 °C, using a high speed blender. The mixing water was either distilled water or a solution of alkalis (sulfates or hydroxides).

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prepared by adding the appropriate sodium and potassium compounds to distilled water and stirring with a glass rod until complete dissolution. Cement 140 is a low-alkali cement, containing only 0.093%Na_2O and 0.186%K_2O per unit mass of cement [6]. For preparing the cement paste with additional alkali in the form of sulfates, 0.76%Na_2SO_4 and 0.93%K_2SO_4 per unit mass of cement were added to the mixing water. This provides a *total* alkali content of 0.42%Na_2O and 0.69%K_2O per unit mass of cement. These contents, and all others prepared in this study, are thus well within the range observed in commercially available portland cements, as for example CCRL proficiency cement samples 141 and 142 contained Na_2O contents of 0.4% and 0.31%, and K_2O contents of 1.04% and 1.08%, respectively [7].

Because the additional sulfates will also modify the phase assemblage produced during cement hydration, additional alkalis were also introduced to the cement paste in the form of hydroxides. For the alkali hydroxides, to maintain the same molar addition rates of the sodium and potassium, 0.43%NaOH and 0.60%KOH per unit mass of cement were added, being sure to account for the quoted 89% purity of the commercially available KOH pellets. To further investigate the influence of the level of alkali addition on the observed results, for the hydroxide additions, cement pastes with 0.14%NaOH/0.20%KOH (low level of additions) and 0.28%NaOH/0.40%KOH (medium level of additions) were also prepared. After mixing, cast wafers ($\approx$5 g) of the paste were placed in sealed plastic vials. A small quantity of distilled water was added to the top of the wafers to maintain saturated curing conditions. The capped vials were placed in a walk-in environmental chamber maintained at 20 °C. At various ages, specimens of the pastes were removed from the vials for further analysis.

Degrees of hydration of the cement pastes, defined as the mass fraction of the original cement that has participated in hydration reactions, were assessed using LOI analysis to measure the non-evaporable water content (W_N) as that quantity removed from the specimens between 105 °C and 1000 °C, corrected for the LOI of the initial cement powder [8]. Previously, the expanded uncertainty in the calculated W_N had been estimated to be 0.001 g/g cement [8]. W_N values 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 hydrated cement clinker phases [9]. Based on a propagation of error analysis, the estimated uncertainty in the calculated degree of hydration was 0.004. For a smaller subset of the specimens, thermogravimetric analysis (TGA) was conducted between 100 °C and 1000 °C at a scan rate of 10 °C/min, with a sample size of about 30 mg.

Small pieces of the hydrated cement pastes were also utilized in the LTC experiments. Sample mass was typically between 30 mg and 90 mg. For each LTC experiment, one small piece of the relevant cement paste was surface dried and then placed in a small open stainless steel pan. The pan with the sample, along with an empty reference

pan of similar mass to the empty sample pan, was placed in the calorimeter cell. Using a protocol developed previously [10], a freezing scan was conducted between 5 °C and −55 °C at a scan rate of −0.5 °C/min. For temperatures between −100 °C and 500 °C, the equipment manufacturer has specified a constant calorimetric sensitivity of ±2.5% and a root-mean-square baseline noise of 1.5 μW.

In this study, the peaks observed in a plot of heat flow (normalized to the mass of the sample) versus temperature are assumed to 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, the presence of, absence of, or change in 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. Specifically, the presence or absence of a "capillary" pore freezing peak near −15 °C is assumed to indicate the percolation or depercolation, respectively, of the capillary pores in a hydrating cement paste [5,10].

The peak at −15 °C is taken to indicate the *percolation* of the capillary pore network and not simply the water freezing in the capillary pores located throughout the cement paste microstructure for the following reasons. In [5], SEM images obtained after 90 d hydration were segmented into four phases and the areas occupied by individual two-dimensional capillary pores (the darkest of the four phases) were determined. The SEM results indicated the presence of a set of large capillary pores ($\geqslant$7.5 μm^2 in area) in a $w/c = 0.35$ hydrated cement paste, even though no peak was present in the range of −15 °C in the LTC scans obtained on equivalent age samples, implying that while these pores are physically present, they are isolated and not part of a percolated (capillary) network. In [10], it was indicated that the disappearance of this peak for cement pastes with $w/c = 0.3$ and $w/c = 0.4$ corresponded to the expected times of depercolation from previous measurements [8,11]. Finally, Villadsen has shown that LTC produces a pore size distribution that is basically equivalent to that obtained with mercury intrusion porosimetry (MIP), when specimens are prepared (dried) equivalently [12]. However, a critical advantage of LTC over MIP and other techniques for assessing pore size and connectivity is that the specimens may be evaluated without any drying that might damage the pore structure. LTC studies with variable alkali content are complicated somewhat by the change in freezing point depression due to the variable ionic concentration of the (freezing) pore solution, and this effect must be considered as well. The maximum initial dosages of alkali sulfates or hydroxides in the cement pastes with additional alkalis prepared in this study would be expected to depress the freezing point of bulk water between 1 °C and 2 °C [13].

3. Results and discussion

The measured LOI-based degree of hydration results for the five cement pastes are provided in Fig. 1. As has been
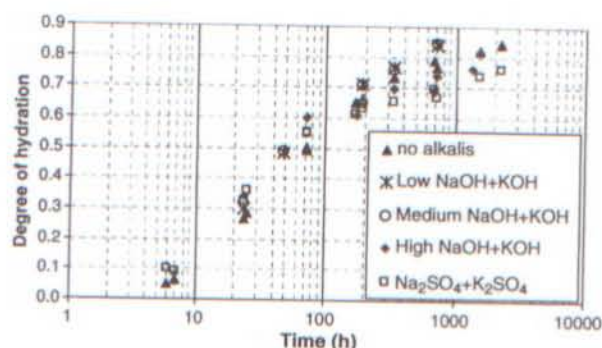
Fig. 1. Degree of hydration via LOI technique for $w/c = 0.40$ cement pastes with and without alkali additions. Each data point is the average of two specimens taken from a single cast wafer at the indicated age.

Fig. 3. LTC results for CCRL 140 $w/c = 0.40$ cement pastes with and without alkali additions cured under saturated conditions for 2 d.

Fig. 4. LTC results for CCRL 140 $w/c = 0.40$ cement pastes with and without alkali additions cured under saturated conditions for 8 d.

observed previously [1,2], the addition of alkalis at high levels accelerates the early age (<7 d) hydration, while retarding the hydration achieved at later ages (28 d and beyond). Interestingly, at an age of around 7 d (150–200 h), the five pastes have similar degrees of hydration as measured by non-evaporable water content. Specifically, the degrees of hydration of the no additional alkali cement pastes and those with the highest level of alkali addition are basically equivalent at 8 d, as are the two values for the low and medium level additions. Furthermore, as shown in Fig. 2, the TGA scans for 8 d old specimens of the paste with no alkali addition and the two pastes with the highest addition levels are basically identical, suggesting that the same amounts of bound water exist in the pastes, both in the C–S–H gel and other hydration products (removed in the temperature range of 100–400 °C) and in the calcium hydroxide (removed in the temperature range of 400–550 °C). The TGA-measured mass loss between 105 °C and 1000 °C was essentially identical (0.176 g/g ignited cement) for the three specimens examined by TGA.

LTC results for the five pastes after 2 d and 8 d of saturated curing are presented in Figs. 3 and 4, respectively. The peaks near −15 °C indicate the presence of a connected or percolated capillary pore system within the three-dimensional paste microstructure [10]. For the 2 d specimens, a prominent peak near this temperature is
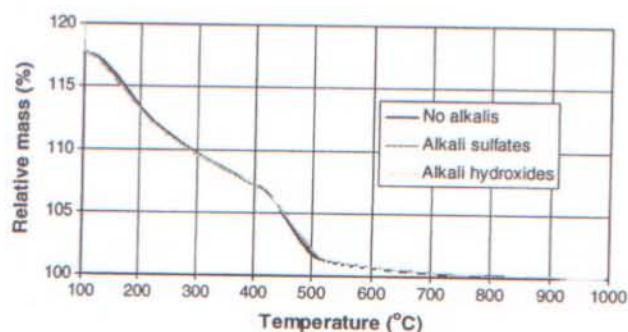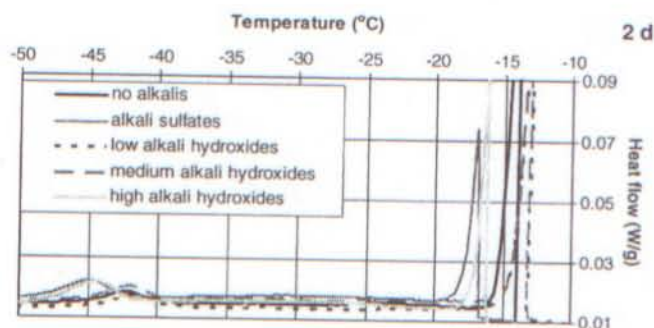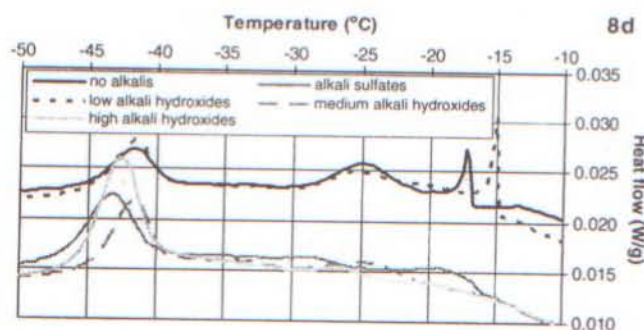

Fig. 2. Relative mass of $w/c = 0.40$ cement pastes versus temperature for specimens with the highest level and without alkali additions hydrated under saturated conditions for 8 d at 20 °C.

observed for all five pastes. The two pastes with the highest levels of additional alkali do indicate some shifting of this peak to lower temperatures by as much as 2–3 °C, as would be expected due to the higher ionic concentrations in their pore solutions. In Fig. 3, the peaks at −40 °C to −45 °C indicate dense gel pores (entryways) within the C–S–H hydration product [10]. Here, the pastes with additional alkalis all exhibit larger peaks, consistent with their higher degree of hydration after 1–3 d (Fig. 1). The more surprising LTC results are to be found in Fig. 4, where *only* dense gel pores are clearly detected for the three specimens with medium and high levels of alkali additions, while the original paste and the paste with the low addition level of alkali hydroxides both exhibit three percolated pore structures corresponding to entryways composed of capillary pores, open gel pores (peak at −25 °C), and dense gel pores [10]. These results imply that the larger open gel and capillary pores in the pastes with higher alkali levels have been depercolated by the hydration products, and at a degree of hydration similar to that achieved in the original paste without additional alkalis and the one with a low level of addition, both of which did not yet achieve depercolation.

This difference in pore space percolation at 8 d for specimens with equal w/c ratios and equal degrees of hydration suggests a difference in either the specific volume or the morphology of the C–S–H gel hydration products. One possibility would be that the presence of substantial numbers of alkali ions in the pore solution and their incorporation into

the C–S–H gel nanostructure leads to a gel with a higher total water content (greater degree of swelling). For example, it is well known that the alkali silica gel (similar in chemical composition to C–S–H [14]) formed in concretes undergoing alkali-silica reaction can be quite expansive. However, in contradiction to this hypothesis, the measured mass losses between 60 °C and 100 °C in the TGA measurements (which can provide some indication of the evaporable gel water) were quite similar for the various pastes, as were their non-evaporable water contents as indicated previously in Figs. 1 and 2. The second possibility would be that the presence of substantial alkalis results in the formation of a C–S–H hydration product with a different morphology than that formed in low alkali cement pastes. Previous electron microscopy observations on tricalcium silicate (C_3S) and portland cement pastes [3,4] have indeed indicated a greater tendency towards plate or lath-like hydration products with a higher degree of crystallinity in the presence of alkalis. Such a product morphology could also reduce long-term hydration, due to either a less permeable, more crystalline layer of C–S–H forming on the remaining unhydrated cement clinker particles or reduced diffusion rates within the pore space. The issue of whether product morphology could indeed affect the percolation of the capillary pores is considered next.

The influence of product morphology on porosity percolation was *preliminarily* examined using a *simple* dissolution/precipitation microstructural model. The model was developed only to consider the possible influence of reaction product morphology on the percolation/depercolation of the "capillary" porosity between the original solid particles (modeled as digitized spheres) in a system that reacts with water via a dissolution/precipitation mechanism. The model is similar to the original pixel-based C_3S hydration microstructural model developed at NIST [15], but with the creation of only one type of reaction product that nucleates and grows as "crystals" in the available water-filled capillary pore space. Portions of the original particles dissolve, diffuse, and precipitate and grow this reaction product. In the model, the three-dimensional morphology of this single reaction product is controlled to be exclusively either one-dimensional needles (one pixel by one pixel across), two-dimensional plates (one pixel thick), or random agglomerates. For computational simplicity, the needles and plates were always oriented along one of the three principal axes (chosen at random), because the model is being executed on a three-dimensional volume that consists of cubic elements (voxels). Here, the model was run with an initial "water-to-solid" mass ratio of 0.40 and an expansion factor of 2.15. The expansion factor is defined as the ratio of the volume of the reaction products to that of the solid reactants; for a typical portland cement, it has a value of about 2.15 [8,10,15]. As the reaction proceeds, the percolation of the pore space is periodically monitored using a simple burning algorithm [15]. Typical results for the connected fraction of the capillary porosity as a function of total capillary porosity are provided in Fig. 5.
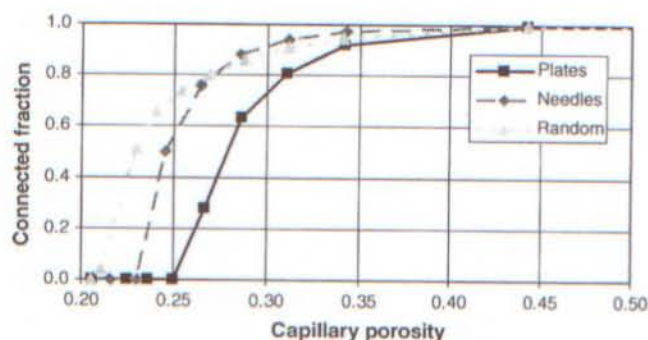

Fig. 5. Dissolution/precipitation model results for capillary porosity percolation (connected fraction) as a function of capillary porosity for different product morphologies (plates, needles, or random) as indicated in the legend. Results shown are the average of 10 separate simulations for each morphology at a $w/c = 0.40$, with an expansion factor of 2.15.

Clearly, in the systems where the reaction product morphology is limited to either needles or plates, the capillary porosity is depercolated at a significantly higher total porosity (equivalent to a lower degree of hydration). The formation of either needle or plate structures is seen to be more efficient at depercolating the capillary pore space than the formation of a random reaction product. This simple model thus supports the experimental observation that the capillary pore space depercolates at a lower degree of hydration in the pastes with sufficient additional alkalis where plate-like hydration products have been observed to be preferable [3,4].

This difference in percolation could potentially have some influence on the transport properties and durability of the cement pastes. For instance, as directly indicated by the LTC results in Fig. 4, at an age of 8 d, the pastes with sufficient (medium or high) additional alkalis will contain little if any freezable water for temperatures down to about −40 °C, which should result in an improvement in freeze/thaw durability relative to the lower alkali cement pastes that contain a measurable amount of water that is freezable at −20 °C and above. Also, as first indicated by Powers et al. [11], there is typically a dramatic decrease in measured fluid permeability as the capillary porosity depercolates. While higher potassium and sodium contents in cements may be unfavorable due to ASR and other concerns, similar effects on the depercolation of the capillary porosity might be achievable by the addition of the lithium admixtures that are conventionally used to mitigate ASR, as lithium ions have been observed to be "the alkali most preferentially incorporated into the cement hydrates" [16]. Current studies at NIST are being directed at examining the influence of lithium additions on achieved hydration and porosity percolation using the techniques presented in this paper.

4. Conclusions

Low temperature calorimetry measurements have indicated that alkalis (present as either sulfates or hydroxides) can have a significant influence on the percolation of the

capillary porosity in hydrating cement paste, possibly via their influence on the morphology of the gel hydration products, increasing the tendency for the formation of lath or plate-like hydration products. At equivalent degrees of hydration (and equivalent ages), pastes with sufficient additional alkalis may exhibit a depercolated capillary pore network, while those present in equivalent w/c, lower alkali cement pastes may remain percolated.

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