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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Keywords: Acceleration; Alkalis; Hydration; Low temperature calorimetry; Percolation

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 (≈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