Elucidating the Effect of Water-to-Cement Ratio on Hydration Mechanisms of Cement

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(A) Cement Composition and Mixing Procedure

A type I ordinary portland cement (OPC) is used in this study. Their composition, as determined from a combination of x-ray fluorescence (XRF) and quantitative x-ray diffraction methods (QXRD) methods, are listed in Table S1. All pastes were prepared at room temperature (23 ± 2 °C). The mixing procedure involved the gradual addition of water to the cementitious material (i.e., cement) followed by hand-mixing (i.e., ≈100 rpm) for 90 sec.

| Phases                          | Oxide composition determined from XRF method | Type I cement |
|--------------------------------|---------------------------------------------|---------------|
|                                | # Mass%                                      |               |
| SiO₂                           |                                             | 19.8          |
| Al₂O₃                          |                                             | 4.5           |
| Fe₂O₃                          |                                             | 3.2           |
| CaO                            |                                             | 64.2          |
| MgO                            |                                             | 2.7           |
| SO₃                            |                                             | 3.4           |
| Na₂O equivalent                |                                             | 2.2           |
| Loss of Ignition (LOI)         |                                             | 2.6           |
| Crystalline phase contents     |                                             |               |
| Alite (C₃S)                    |                                             | 61            |
| Belite (C₂S)                   |                                             | 8             |
| Aluminate (C₃A)                |                                             | 6             |
| Ferrite (C₄AF)                 |                                             | 9             |
| Gypsum (C$H₂)                  |                                             | 3.4           |

(B) 3D Microstructural Model

To generate 3D microstructures of cementitious systems, a 3D microstructural model, which has been used previously to study the effects of various process parameters on the evolution of the microstructure of various plain and blended cement-based systems¹⁻⁸, was used. The model implements a vector approach⁹ in conjunction with particle packing and microstructural development algorithms, to reproduce the evolution of the microstructure as driven by chemical
reactions between the solid precursors (e.g., cement) and water. The model uses the measured (or calculated) PSDs and volumetric fractions of the components of the system (i.e., cement and water) as inputs. A particle packing algorithm is then employed to generate a 3D cubic representative elementary volume (REV: the size of which is defined by the user), wherein the solid phases, represented as spheres corresponding their original PSD, are randomly dispersed and packed following periodic boundary conditions within the REV. The volume of the REV not occupied by the solid spheres is left empty to represent water. Next, to simulate the evolution of the microstructure as the reaction progresses, the degree of hydration of cement (DOH) is used as an input, and based on the amount of cement reacted, the corresponding amount of hydrates formed is represented as a combination of layered-hydrates (i.e., nuclei formed on the receding anhydrous particles) and discrete-hydrates (i.e., new spherical grains formed in the empty pore space). The scheme of distribution of the overall volume of the hydrates into layered- and discrete-hydrates is implemented to mimic both heterogeneous (e.g., nucleation of C-S-H on cement particles’ surfaces) and homogeneous (e.g., nucleation of CH in the pore space) forms of nucleation of hydrates, as observed in microstructures of cement pastes\(^1,7,10\). The distribution of the hydrate volume into layered- and discrete-hydrates is fixed throughout the simulations. Specifically, for every unit volume (expressed as cm\(^3\)) of hydrates formed, 60% and 40% of the overall hydrate volume are assigned to layer- and discrete-hydrates, respectively. This scheme of division of the hydrate volume is based on the hydration reaction of C\(_3\)S with water, which results in the formation of C-S-H and CH, wherein C-S-H occupies \(\approx60\%\) of the overall volume of hydrates and grows heterogeneously on the surfaces of C\(_3\)S particles, whereas CH amounts to \(\approx40\%\) of the
overall hydrate volume and grows in the capillary pore space\textsuperscript{1,11–14}. As reaction progresses, both layered- and discrete-hydrates are allowed to grow, in relation to their volumetric increase (based on amount of cement reacted). Therefore, at any given degree of hydration (DOH), a virtual microstructure is generated, which consists of anhydrous (i.e., unreacted precursor materials) particles, layered- and discrete-hydrates, and pores. An example of this is shown in Figure S1. In Figure S1, as well as the simulations presented in the manuscript, the cement is assumed to be a standard type I portland cement, with an estimated Bogue phase composition as listed in Table S1. The overall quantity of hydrates formed as a result of the hydration of cement, and the corresponding capillary porosity (i.e., unoccupied space in the microstructure), are described as per the formulation used in the Powers model\textsuperscript{15,16}.

![Figure S1: Virtual 3D microstructures of cement paste prepared at l/s = 10 at DOH (α) of: (a) 0, (b) 0.20, and (c) 0.60. The anhydrous cement particles are represented in red, and packed within the cubic REV (size = 100 µm\textsuperscript{3}) as randomly dispersed spheres with sizes drawn directly from the input PSD. As cement reacts with water and hydrates are formed, the hydrates are allowed to grow as layered-hydrates (blue) and as discrete-hydrates (green).](image)

\*The volume of C-S-H and CH formed per unit volume of C\textsubscript{3}S reacted depend on the assumptions of the molar mass (or composition) and the density of C-S-H. Here, the molar mass and density of C-S-H were assumed as 227.2 g/mol and 1.97 g/cm\textsuperscript{3}, respectively.
(C) Isothermal Microcalorimetry

A TA Instruments TAM IV Microcalorimeter was used to determine the time-dependent reactivity of cement. Compared to conventional methods of reactivity assessment (e.g., isothermal calorimetry), microcalorimetry methods offer a number of unique advantages that enable rapid, direct, and precise measurement of time-dependent reactivity of materials. Some key advantages include: (a) quantification of heat flow-rate/release of reaction at very high resolution (10^{-7} \text{J/s}), which enables monitoring dissolution of very slow (e.g., silicates) and very fast (e.g., cement) dissolving compounds even at high dilutions (e.g., l/s = 10000), and (b) a built-in injection kit and a magnetically-driven stirrer for “in-situ” studies of solute-solvent interactions, all while the system is continuously stirred^{8,17–19}.

**Figure S2:** (a) A schematic of the titration cell of the microcalorimeter. The cell is fitted with an electrically-driven agitator which allows in-situ mixing of hydrating pastes. (b) Heat release and heat flow rate associated with the mixing of DI-water in the titration cell. The rotational speed of the agitator was fixed at 80 rpm.
To quantify the time dependent reactivity of cement (i.e., degree of hydration: \( \alpha \)) using isothermal microcalorimetry, the experimental protocols, as well as the methods of analyses, are identical to those used in conventional isothermal calorimetry methods\(^3,13\). Specifically, the cumulative and differential heat release (resulting from the exothermic heat release of cement-water interactions) are normalized by the enthalpy of cement hydration, 472 J. g\(_{\text{cement}}\)^{-1}, to derive the extent of reaction (\( \alpha \)) and the rate of reaction (\( \frac{d\alpha}{dt} \)), respectively, as functions of time\(^1,13,19\). For plain cement pastes prepared at \( l/s = 0.45 \), the values of \( \alpha \) determined from isothermal calorimetry and isothermal microcalorimetry were compared, and found to be within \( \pm 1\% \) of each other.

Selected experiments presented in the paper were carried out using the titration cell (Figure S2a). As can be seen, the cell is fitted with an electrically driven agitator that allows in-situ mixing of the hydrating pastes that are prepared at high w/c. The turbine-shaped blades of the agitator are gold-plated, and, therefore, do not partake in chemical interactions with any of the paste components. However, on account of the mixing action (i.e., shear force between the blades of the agitator and paste components), a finite, albeit small, amount of heat is released. To isolate and quantify the heat associated exclusively with the mixing action, experiments were carried out using DI-water (and no cement), while rotating the agitator at a constant speed of 80 rpm over the course of 24 h. As shown in Figure S2b, \( \approx 0.15 \)J of heat is released due to the mixing action between the agitator’s blades and water, which is considerably smaller than the heat release associated with the highly exothermic interactions between cement and water.
(D) Sensitivity of pBNG Parameters

Figure S3 shows the sensitivity of the pBNG simulations with respect to variations in the reactive paste fraction parameter (pf).

In Figure S3, simulations were employed in two steps, using SSA$_{\text{cem}}$ = 196 m$^2$. kg$^{-1}$, l$_{\text{density}}$ = 3.50 µm$^{-2}$, g = 0.25, r$_G$ = 0.50, and keeping the product growth rate (G$_{\text{out}}$) constant at 0.075 µm. h$^{-1}$ throughout the simulations (i.e., akin to classical pBNG models). In Figure S3a and S3b, the values of w/c were varied over a wide range while keeping the values of other parameters fixed. In Figure S3c, simulations were employed in a similar manner, except that the w/c was kept constant at 3.00 and the parameter pf was allowed to vary over a wide range. As can be seen in Figures S3a-S3b, at larger values of w/c (and pf = 1.00), the enlargement of reaction vessel and reduction of a$_{\text{BV}}$ (Eq. 6) ensure larger spacing between the cement particles and fewer impingements between product nuclei; this results in slower approach to the main hydration peak and, more importantly, slower decline in the hydration rate after the peak. These results qualitatively show that at higher w/c, if the entire reaction vessel is assumed to participate in the nucleation and growth process, the hydration rates estimated from the pBNG simulations (shown in Figure S3b) are significantly different compared to those obtained from experiments (Figures 2-3). However, by restricting the size of the reaction vessel (i.e., by using pf < 1, as shown in Figure S3c), a$_{\text{BV}}$ increases and the effective w/c (i.e., w/c$_{\text{RV}}$) reduces; on account of these changes, the impingements between product nuclei amplify, and, as such, the simulated rates of product formation (expressed as dX/dt) of higher w/c pastes exhibit trends similar to those of lower w/c pastes (see the grey curves in Figures S3a and S3c). It is important to note that optimization of pf
only provides good fits between the rates of product formation (i.e., $dX/dt$) of the simulated and measured hydration profiles. Optimization of the $[G_{out}(t)]$ – which is employed in the final step of the simulations using the Nelder-Mead simplex approach – is needed in the next (and final) step to match the net reaction rates (expressed as $d\alpha/dt$) of the simulations with the experiments.

Figure S3: Simulations demonstrating the sensitivity of the pBNG simulations conducted using constant $G_{out}$ of 0.075 $\mu$m. $h^{-1}$, $I_{density} = 3.50 \mu$m$^{-2}$, $g = 0.25$, $r_G = 0.50$, $SSA_Cem = 196 \ m^2. \ kg^{-1}$. Variations in (a) $dX/dt$ (i.e., rate of product formation, or the derivative of Eq. 1) and (b) $d\alpha/dt$ (i.e., rate of reaction or the derivative of Eq. 8a) with respect to w/c while keeping $p_r$ constant at 1.00. (c) shows variations in $dX/dt$ with respect to $p_r$ while keeping w/c constant at 3.00.

(E) Heat evolution profiles of Water-Deficient Pastes

Figure S4 shows the heat flow rates and cumulative heat release of pastes prepared at w/c < 0.42. For comparison, heat evolution profile of a water-rich paste, i.e., w/c = 10, is also shown. As can be seen, even in water-deficient pastes, the hydration kinetics are broadly insensitive to changes in the w/c, akin to pastes prepared with excess water (i.e., w/c > 0.42).
Figure S4: (a) Isothermal microcalorimetry based determinations of (a) heat flow rates, and (b) cumulative heat release of water-deficient pastes prepared using the coarse cement. For comparison, heat evolution profiles of a water-rich paste prepared at w/c = 10 is also shown.

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