

# Early Hydration: a local business

## Problem

The kinetics of portland cement hydration has been actively researched for decades as it controls the setting and hardening of concrete, both of which are central to engineering practice. Many factors influence the hydration rate, including the particle size distribution (PSD) of the cement powder and the addition of chemicals, while other variables such as water/cement ratio (w/c) affect mechanical properties but have limited influence on kinetics. Present models have difficulty simultaneously capturing the influence (or lack of influence) of PSD and w/c on kinetics. The reason is that the end of the early hydration period has been generally assumed to occur when all of the available pore volume fills with hydration product. By contrast, a newly proposed scenario where the early hydration product grows only within a “reaction zone” extending a few micrometers from the surface of the cement particles can explain and reconcile many experimental observations including effects of PSD and w/c. This is important, because a more complete understanding of the local processes of nucleation and growth could lead to new strategies to tailor the early hydration of cement, controlling also the effect of additives, seeds, and supplementary materials.

## Approach

A new microstructure-based kinetics (MBK) model has been developed (see also the CSHub Research Brief of November 2011). To save computation time, the MBK model treats the

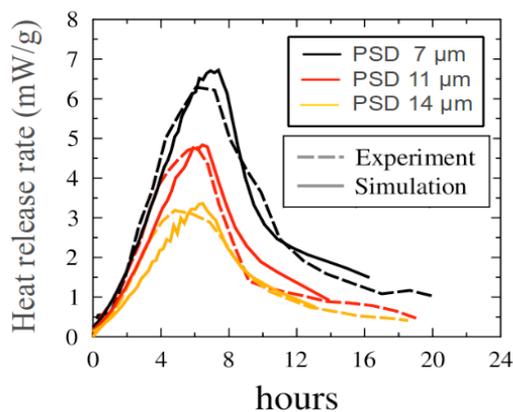


Fig. 1: Calorimetry curves from experiments on  $C_3S$  pastes (Garraut et al. *J. Phys. Chem. B* 2006) and from our model with a reaction zone thickness of  $\sim 0.4$   $\mu\text{m}$  (Masoero et al. *J. Am. Ceram. Soc.* in press). The pastes have high water-to-cement ratio  $w/c = 50$ . The effect of cement particle size distributions (PSDs) with mean size of 7, 11, and 14  $\mu\text{m}$  is captured well.

cement particle size distribution and the spatial distribution of particles in the suspension in a statistical way. Early hydration is simulated as essentially a boundary nucleation and growth process where hydration product forms initially at the surface of the cement particles. Finally, the reaction zone hypothesis was implemented by allowing the early hydration product to form only within a certain prescribed distance from the surface of the cement particles in suspension.

## Findings

The MBK model was used to fit kinetic data from two published studies for  $C_3S$  (the main cement mineral), one for pastes and one for dilute, stirred suspensions. Both studies used powders with different PSDs and found that when the particles are smaller, the rate of heat release (directly proportional to hydration rate) is faster and a greater amount of hydration product is produced during the first 24 hours after mixing (see Fig. 1, solid lines). The MBK model was able to fit the kinetics accurately in all cases (Fig. 1, dashed lines). Importantly, for a given study, the fitted values of the reaction zone do not depend on the PSD, which is the expectation if the concept is physically valid. For the pastes, the reaction zone size is about 0.5  $\mu\text{m}$ , while for the suspensions the size is about 1  $\mu\text{m}$ , as measured from the surface of the particle. Another important observation, observed in numerous studies, is that the water/cement ratio has little effect on the kinetics. This is difficult to reconcile with a pure nucleation and growth process, which predicts impingement of hydration product inside the pore space to generate the observed hydration rate peak. However, the weak effect of water/cement ratio is a natural consequence of the reaction zone, as shown by the MBK model.

We found that the reaction zone size is correlated with the formation of a compact layer of hydration product around the cement particles. This suggests that the physical origin of the reaction zone could lie in local variations of the ion supersaturation levels, which provide the driving force for product growth.

## Impact

A new reaction zone hypothesis reconciles a number of experimental observations on the early hydration kinetics of cement. The new MBK simulation model provides a tool for exploring the relationship of admixtures (seeds, additives, and supplementary materials), to reaction kinetics and to the distribution and structure of reaction products throughout the microstructure of cement based materials.

## More

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