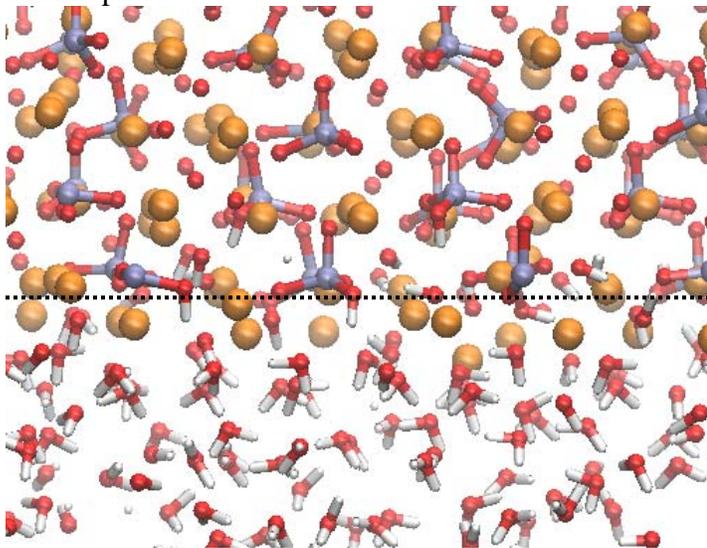


ReaxFF Hydration of Clinker Surfaces

Problem

What drives the onset of cement hydration, pore solution chemistry or clinker crystallinity? – The question has haunted cement chemists for many years; and it has gained new prominence in the current research and development of cements with low carbon footprint. Answering this question is particularly important for controlling the properties of hydrating cement from its inception, including the activation of lower energy clinker phases such as belite. Yet, despite years of experimental research, the onset of alite and belite dissolution is still an enigma that cannot be resolved by classical close-to-equilibrium thermodynamics approaches. In such a situation, atomistic simulation is a valuable tool to provide detailed information about the chemical mechanisms that take place at the solid-water interface. Such atomistic simulation must be able to simulate the crystal bond breakage and bond formation that control the early stage reactivity of clinker phases.



Snapshot of alite {001} surface after 1 nanosecond of contact with bulk water: Water dissociates at the surface to form OH groups. Hydrogen atoms then “jump” from oxygen to oxygen penetrating the crystal, while calcium is released into the solution. The orange, blue, red and white spheres represent Ca, Si, O, and H respectively, and the dotted line is the initial position of the alite surface.

Approach

The study of chemical reactions of large systems over large time scales is difficult: quantum chemistry approaches are computationally too intensive, while molecular dynamics using simple empirical potentials cannot reproduce chemical reactions with the necessary accuracy. To overcome these limitations, we employ a reactive force field approach, ReaxFF, which incorporates into the force field expressions additional terms to capture bond breakage and formation. In particular, we developed a new reactive force field for calcium containing systems, which permits the accurate study of the reactivity of water-clinker interfaces using atomic scale simulations.

Findings

The main chemical mechanism that defines the onset of clinker hydration is water dissociation, which is triggered by the diffusion of protons (hydrogen atoms) into the crystal. Water dissociation is found to be considerably slower on belite surfaces than on alite surfaces. This provides evidence that the difference in reactivity is intrinsic to the crystal; and hence independent of the equilibrium with the pore solution.



Impact

This research highlights that the difference in reactivity of alite and belite is inherent to their crystalline structure. This means, from a dissolution kinetics perspective, that a shift from an alite to belite dominated system can be achieved by crystal modifications and surface engineering. The insight thus gained with ReaxFF can enable R&D of clinker phases with higher reaction rates and early strength development.

More

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