

Microscopic Modeling of Silicate Speciation Using Reactive Monte Carlo Simulations

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The accurate determination of intrinsic equilibrium constant values for silicate oligomers remains a fundamental challenge in aqueous silicate systems. Reported equilibrium constants for the silicate oligomerization and deprotonation reactions show significant variation, largely due to differences in the experimental conditions and ionic strength [1]. In addition to these experimental factors, much of this spread also arises from the limitations of conventional speciation models such as GEMS and PHREEQC. These models rely on the Debye-Hückel approximation, which treats ions as point charges and does not account for crucial intramolecular interactions that influence the reactivity and stability of silicate oligomers. This limitation is particularly acute in cement carbonation processes, where precise knowledge of silicate and aluminate speciation equilibria is essential for predicting dissolution rates and secondary phase formation during calcium-alumino-silicate-hydrate (C(A)SH) carbonation [2].

This study addresses these limitations through reactive Monte Carlo (RMC) simulations combined with a coarse-grained atomistic model of silicate species. The approach represents silicate monomers as spheres, while oligomers are modeled as connected spheres, with explicit Coulombic interactions and hard-sphere potentials to capture both electrostatic and steric intramolecular effects, while treating water as a dielectric continuum to approximate solvation.

By bridging molecular-level interactions and macroscopic thermodynamics, this approach sets a new standard for silicate equilibrium modeling and delivers the precise speciation data needed to predict dissolution rates and secondary phase formation during C(A)SH carbonation.

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