Development and Characterization of β-Dicalcium Silicate Nanoparticles for Greener Cementitious Materials

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Abstract

Cement manufacturing is responsible for approximately 5% of the world's carbon dioxide (CO_2) emissions, due to the release of CO_2 from limestone ($CaCO_3$) during high-temperature calcination to yield CaO. CaO is used as a source of calcium cations during the formation of anhydrous cement powders, which are comprised of calcium silicates and aluminates with typical particle sizes of several microns. The major components of anhydrous cement powders are *tri*calcium silicate (Ca_3SiO_5) and *di*calcium silicate (Ca_2SiO_4), which are responsible for the development of mechanical strength properties as cements hydrate. Though they are chemically similar, they hydrate at dramatically different rates: *tri*calcium silicate hydrates over days to weeks, compared to *di*calcium silicate which typically hydrates over months and years, due to its intrinsically slower hydration kinetics and large particle sizes. Increasing the overall hydration rate of *di*calcium silicate is considered to be an attractive option for replacing a portion of the *tri*calcium silicate to achieve similar mechanical strength properties with lower total calcium contents. Correspondingly, this could reduce the carbon foot print of the cement manufacturing process.

Recently, we have synthesized β-*di*calcium silicate by using a sol-gel process, rather than by the conventional solid-state reaction, to yield small (ca. 100 nm) Ca_2SiO_4 particles that hydrate much more rapidly: 85% complete within 30 days, compared to 20 days for conventionally prepared (micron sized) Ca_3SiO_5. By comparison, β-*di*calcium silicate synthesized using the conventional approach typically reach 85% hydration in about 180 days. The increased rate of hydration is thought to be due principally to the smaller particle sizes. Solid-state ^{29}Si nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM) provide new understanding of the molecular structures and compositions of β-dicalcium silicate before and after hydration. In particular, solid-state ^{29}Si NMR spectra allow the mean lengths of hydrating silicate chains to be determined, as functions of particle size, preparation conditions, and extent of hydration. The analyses yield detailed molecular insights that are correlated with macroscopic properties, such as the viscosities and compression strength of hydrating slurries that help to understand the development of mechanical strength in cement materials.