Unravelling the Atomic-level Structure of Calcium Silicate Hydrate

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Calcium silicate hydrate (CSH) is one of the most versatile and widely used substances worldwide. The main use of CSH is as primary binding component in concrete, where it forms about 50-60% by volume of the dried cement paste [1]. With cement being the most widely used construction material, so abundant that its production is the leading industrial source of greenhouse gases, contributing to about 8% of global emissions, a deep knowledge of the structure of CSH is of global priority.

Other emerging applications of CSH range from usage in dental fillings and bone repair, requiring biocompatibility, to waste water treatment, requiring a high specific surface area, to encasement of nuclear waste, requiring high structural integrity. Despite the versatile and frequent usage of CSH it is surprising that the full atomic-level structure of CSH remains unknown [2,3].

The main reasons for the unresolved atomic-level structure of CSH arise from the fact that CSH always is slightly disordered, that it occurs in nature in conjunction with other materials phases, and that previously synthetic CSH could only be produced with Ca:Si ratios below 1.6, whereas the industrially relevant ratio is greater than 1.75 [4]. Here we present a novel method which achieves the synthesis of uniform CSH phases with Ca:Si ratios between 1.0 and 2.0. We then solve the three-dimensional atomic-level structure using an approach combining dynamic nuclear polarization (DNP) enhanced solid state nuclear magnetic resonance (ssNMR) experiments, molecular dynamics (MD) simulations and chemical shift calculations based on first principle.

To solve the atomic-level structure of CSH we first determine structural constraints through one- and two- dimensional ^{29}Si DNP cross polarization ssNMR experiments, employing magic angle spinning (MAS) of the sample. These constraints, in combination with force-field based MD simulations, are then used to generate an ensemble of possible short range building blocks for the CSH structure. By combining these building blocks we then generate a set of medium to long range structural motifs, which we optimize using density functional theory (DFT). We then compare the DFT calculated ^{1}H chemical shifts of these motifs with experimentally measured two-dimensional {^{1}H}^{29}Si DNP HETCOR chemical shifts to determine the subset of structures that best describe the CSH structure. This subset in combination with additional structural constraints, resulting from the ^{29}Si chemical shift experiments, and MD simulations then allow us to propose a full atomic-level structure of CSH.

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