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# Improving the structural consistency of C-S-H solid solution thermodynamic models

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ABSTRACT

Simple aqueous–solid solution models of C-S-H (calcium silicate hydrate) are widely used in studies of cement hydration and waste–cement interactions. Even without a clear structural/mechanistic basis, such thermodynamic models yield a good description of solubility data in [Ca]-C/S space, while only satisfactory in [Si]-C/S, $H_2O$-C/S, [Ca]–[Si] spaces and in the $0.1<C/S<0.8$ range. Here, using a multi-site (sublattice) concept, the ideal solid solution model of C-S-H is revised to make it consistent with the Richardson–Groves structural model of C-S-H and with the modern interpretation of spectroscopic ($^{29}$Si MAS NMR) and solubility data. Consideration of two site substitutions, (1) coupled $H_2OCa^{2+}$ for $SiO_2H_2^{2+}$ replacement in bridging tetrahedral and adjacent interlayer sites, and (2) substitution of interstitial $Ca(OH)_2$ for a vacancy, leads to a new CSHQ model of (A,B) (C,D)X type composed of two tobermorite-like and two jennite-like end members. Because this ideal sublattice SS model cannot fit solubility data well at $0.8<C/S<1.1$, a simpler CSH3T model is constructed from a polymeric TobH $(CaO)_2(SiO_2)_3(H_2O)_5$, a dimeric T2C $(CaO)_3(SiO_2)_2(H_2O)_5$, and an ordered pentameric T5C $(CaO)_{2.5}(SiO_2)_{2.5}(H_2O)_5$ tobermorite-like end members. This solid solution model, limited to the range $0.67<C/S<1.5$, has a correct built-in dependence of the mean silicate chain length on C/S, yields quite realistic fits to the solubility data, and provides a basis for extensions with foreign cations whose sites in the defect-tobermorite structure of C-S-H are known. To account for C-S-H compositions with $C/S>1.5$, CSHQ end members were downscaled to one tetrahedral site and used within the simple mixing model. Despite some loss of structural consistency, the solubility and mean silicate chain length data can be reproduced well with this downscaled CSHQ model, capable of temperature corrections and dependencies of density and water content in fully-hydrated C-S-H on C/S ratio. Most literature solubility data sets can be modeled at the cost of moderate adjustments of CSHQ end-member solubility products within 0.2 to 0.6 pK units.



## 1. Introduction

Knowledge of the solubility and stability of calcium silicate hydrates (C-S-H) is important because the C-S-H formation and structure determine hardening process and strength of cement, and play the major role in cement degradation [1]. Ubiquitous C-S-H gel-like phase is the main sorbent for Na, K and hazardous cations in hydrated cements used in engineered barriers of (nuclear) waste repositories [1–6].

C-S-H has variable composition and shows an incongruent solubility upon de-calcification, re-calcification, carbonation and

*Abbreviations:* Aq-SS, Aqueous solid solution (model); BT, Bridging tetrahedral site (in sublattice C-S-H models); BTI, Bridging tetrahedral interlayer combined site (in simplified sublattice models); C curve, Solubility [Ca]–[Si] eye-guide curve for $C_3S$ hydration samples [18]; C" curve, Solubility [Ca]–[Si] curve for double-decomposition C-S-H samples [18]; C3S, Tricalcium silicate, $Ca_3SiO_5$; CEF, Compound energy formalism (based on the sublattice concept); CH, Portlandite, $Ca(OH)_2$; CL, Chain length (of silica 'dreierketten'); <CL>, mean chain length; C-S-H, Calcium silicate hydrate (gel-like phase); CSH3T, Ternary solid solution model for C-S-H of tobermorite-like structure; CSHQ, Quaternary solid solution model for C-S-H of tobermorite–jennite-like structure; CU, Calcium hydroxide unit (in sublattice models); C/S, Calcium to silicon (mole ratio in the solid part of the system); GEM, Gibbs energy minimization; GEMS, GEM-Selektor geochemical modeling package (http://gems.web.psi.ch); H/S, $H_2O$ to $SiO_2$ (molar) ratio in bulk solid; IC, Interlayer cation site (in sublattice models); IW, Interlayer water site (in sublattice models); J2, Dimeric half-protonated jennite-like end member; J2C, Dimeric jennite-like end member with full interlayer $Ca^{2+}$ occupancy; JenH, Jennite-like end member with $H^+$ (without $Ca^{2+}$) in the interlayer; LDH, Layered double hydroxide; MAL, Mass-action law; MAS, Magic angle spinning; NMR, Nuclear magnetic resonance; RG, Richardson and Groves' (structural model of C-S-H); RH, Relative humidity (in percent for a given temperature); SH, Amorphous hydrous silica $SiO_2$ phase; SS, Solid solution; T2, Dimeric half-protonated tobermorite-like end member; T2C, Dimeric tobermorite-like end member with full interlayer $Ca^{2+}$ occupancy; T5C, Pentameric tobermorite-like end member with full interlayer $Ca^{2+}$ occupancy; T/CH, Tobermorite/Interstitial calcium hydroxide (structural concept); T/J, Tobermorite/Jennite (structural concept); TGA, Thermogravimetric analysis; TU, Tobermorite (structural calcium silicate) unit (in sublattice models); TobH, Tobermorite-like end member with $H^+$ (without $Ca^{2+}$) in the interlayer; $V_{CH}$, Vacancy (of CH on the CU sublattice site), similarly $V_{BT}$, $V_{IW}$; XAS, X-ray absorption spectroscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; [M], Total molarity of aqueous dissolved ionic M (mol $dm^{-3}$).

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