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A thermodynamic model for C-(N-)A-S-H gel: CNASH_ss. Derivation and validation

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Abstract

The main reaction product in Ca-rich alkali-activated cements and hybrid Portland cement (PC)-based materials is an calcium (alkali) aluminosilicate hydrate (C-(N-)A-S-H) gel. Thermodynamic models without explicit definitions of structurally-incorporated Al species have been used in numerous past studies to describe this gel, but offer limited ability to simulate the chemistry of blended PC materials and alkali-activated cements. Here, a thermodynamic model for C-(N-)A-S-H gel is derived and parameterised to describe solubility data for the CaO-(Na_2O,Al_2O_3)-SiO_2-H_2O systems and alkali-activated slag (AAS) cements, and to chemical composition data for C-A-S-H gels. Simulated C-(N-)A-S-H gel densities and molar volumes are consistent with the corresponding values reported for AAS cements, meaning that the model can be used to describe chemical shrinkage in

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these materials. Therefore, this model can provide insight into the chemistry of AAS cements at advanced ages, which is important for understanding the long-term durability of these materials.

Keywords

B. Calcium-Silicate-Hydrate (C-S-H); B. Thermodynamic Calculations; D. Alkali Activated Cement; D. Blended Cement; E. Modelling.

Nomenclature

a	Extent of substitution of trivalent cation *R* in bridging sites
$\dot{a}$	Ion size parameter in the extended Debye-Hückel equation (Å)
a', b', ..., e'	Stoichiometric coefficients in the additivity method
A_γ	Temperature-dependent electrostatic parameter in the extended Debye-Hückel equation
BCI	Combined BT, CB and IC sites ($BCI = BT + CB + IC$)
b^{sc}	Neutron scattering length (m)
BT	Bridging tetrahedra
B_γ	Pressure-dependent electrostatic parameter in the extended Debye-Hückel equation
b_γ	Short-range interaction parameter in the extended Debye-Hückel equation, kg·mol^{-1}
c	Charge of the charge-balancing interlayer cation
CB	Interlayer charge-balancing species for bridging tetrahedra
CL	Chain length of an end-member in the sublattice solid solution model
Cp^o	Absolute isobaric heat capacity at standard state (J·mol^{-1}·K^{-1})
CU	Interstitial 'solid solution' $Ca(OH)_2$
d_1, d_2	Coefficients for the CB sites
e_1, e_2	Coefficients for the IC sites
$\Delta_f G^o$	Standard Gibbs free energy of formation (J·mol^{-1})
G_m	Gibbs free energy of mixing (J·mol^{-1})
G_m^E	Excess Gibbs free energy of mixing (J·mol^{-1})
h	The amount of water per dreierketten unit in a tobermorite-like structure
$\Delta_f H^o$	Standard enthalpy of formation (J·mol^{-1})

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i	Species of the sublattice solid solution model
I	Ionic strength of the aqueous electrolyte phase in the extended Debye-Hückel equation, mol·kg^{-1}
I, II, III, IV, V, VI	Stoichiometric coefficients of the sublattice sites in the solid solution model
$i_1i_2i_3\ldots i_s$	End-member of the sublattice solid solution model written in terms of the species substituted in sublattice sites 1, 2, 3,…, s
IC	Interlayer charge-balancing species for the TU sites
IW	Interlayer water
k	End-member of the sublattice solid solution model
K_{so}	Solubility product
l	Charge-balancing interlayer cation
MW	Molecular weight (g·mol^{-1})
N_A	Avogadro constant (6.022 x 10^{23} mol^{-1})
n_s	Sublattice sites
R	Trivalent cation in tetrahedral coordination
R^*	Universal gas constant (8.3145 J·mol^{-1}·K^{-1})
s	Index of sublattice site n
S^o	Absolute entropy at standard state (J·mol^{-1}·K^{-1})
T	Temperature (K)
TU	Main chain site, $CaSiO_{3.5}^-$
u	Interlayer H^+ content per dreierketten unit for the TU sites
U	Term containing the Gibbs free energies for the reciprocal reactions (J·mol^{-1})
V^o	Standard molar volume (J·bar^{-1})
x_{jw}	Molar quantity of water in the extended Debye-Hückel equation, mol
X_w	Total molar amount of the aqueous phase in the extended Debye-Hückel equation, mol
y_i^{ns}	Site fraction of species i in the sublattice site n_s
z_j	Charge of aqueous species j
α_k	Activity of end-member k
γ_j	Activity coefficient of aqueous species j
$\Delta_{rcp}{}^oG$	Standard Gibbs free energy of a reciprocal reaction between end-members of the sublattice solid solution model
ζ	Stoichiometric coefficient of the s^{th} sublattice site
λ_k	Fictive activity coefficient of end-member k
μ	Chemical potential (J·mol^{-1})
v	Fraction of bridging site vacancies per dreierketten unit
ρ'	Density of an end-member of the sublattice solid solution model (g·m^{-3})
ρ^{sc}	Neutron scattering length density (m^{-2})
Φ^o	Standard thermodynamic property estimated by the additivity method
$\chi_k^{i,ns}$	Effective mole fraction of end-member k containing species i in sublattice site n_s

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1. Introduction

A key factor governing the long-term performance of any cement or concrete is the stability of the reaction products constituting the solid binder. Work in this area has historically been targeted at understanding the chemistry of the primary reaction product in Portland cement (PC) materials, which is a Ca-rich (Ca/Si > 1.5) calcium silicate hydrate (C-S-H)[a] gel [1]. A substantial amount of this research has been devoted to understanding the solubility of C-S-H gel [2-16], and development of thermodynamic models for this phase has been ongoing over the past decades [15, 17-22]. The Kulik and Kersten C-S-H thermodynamic model [17] has been applied extensively to successfully predict hydrated PC solid phase assemblages and pore solution compositions as a function of the bulk solid binder chemistry [23, 24]. The majority of published solubility data for C-S-H gel have been identified to fall onto several distinct solubility curves [8, 16], indicating that an important and complex structure-solubility relationship exists for this phase. More recently, a structurally-consistent C-S-H thermodynamic model has been developed [25], which has further improved the utility of the thermodynamic modelling approach in understanding the chemistry of PC materials.

Although the chemistry of hydrated neat PC materials is now relatively well established, many modern cements are comprised of blends of PC with Al-containing supplementary cementitious materials (SCMs), which react to form calcium aluminosilicate hydrate (C-A-S-H) gels with significantly lower Ca content (Ca/Si ≤ 1.5) [26, 27]. The level of Ca in the gel is reduced even further in alkali-activated slag (AAS) cements, which are formed through the reaction between ground granulated blast furnace slag (GBFS) and a highly alkaline solution (which are most often Na-based, although the products of activation with alternative alkalis such as K are generally similar [28]). The compositions of the C-A-S-H type gels formed in these cements (denoted C-(N-)A-S-H to reflect the

[a] Cement chemistry shorthand notation is used throughout the text: A, Al_2O_3; C, CaO; S, SiO_2; H, H_2O; and N, Na_2O.

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increased alkali content in addition to the high levels of Al incorporated into this phase) vary depending on the activation conditions, but are typically close to Ca/Si = 1 [29].

Previous thermodynamic studies of PC/SCM blended cements [26, 30] and AAS cements [31] have utilised empirical descriptions of Al substitution in C-A-S-H and C-(N-)A-S-H gels (e.g. by attributing amounts of Al to these gels to match experimentally measured Al/Si values of the solid binders in the materials), or have neglected to account for the uptake of Al into these phases in the modelling performed, because existing C-S-H thermodynamic model formulations do not contain explicit definitions of Al [15, 17, 18, 21, 25]. The ability to formally account for the extent of Al incorporation into these models is important because it offers scope to significantly improve the level of detail and confidence in predictions of the solid phases formed in the CaO-Al_2O_3-SiO_2-H_2O system as simulated by thermodynamic modelling. Hence, the development of thermodynamic models with explicit descriptions of Al in C-A-S-H and C-(N-)A-S-H gels signifies an important advancement in how cementitious materials are modelled and understood.

Here, a thermodynamic model is proposed to account explicitly for the tetrahedral Al and Na species bound in C-(N-)A-S-H gel, and applied to simulate the chemistry of AAS cements as an initial example. This model may also be applicable to high-volume blended PC/SCM materials (e.g. CEM III blast furnace cements specified under the EN 197-1 standard) because the structurally-bound Al and alkali species are specified independently in the model formulation, and because the C-(N-)A-S-H and C-A-S-H gels formed in these materials and in AAS cements are similar in nanostructure and chemical composition [26].

2. The chemistry of AAS cements

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C-(N-)A-S-H gel, which is the dominant reaction product in AAS cements, contains aluminosilicate chains arranged similarly to the disordered tobermorite-like phase C-S-H(I) [1], flanked on either side by an 'interlayer' comprised of H_2O and aqueous cations (e.g. Ca^{2+}), and a Ca-O sheet (Figure 1). These aluminosilicate chains are comprised of substituted 'dreierketten' units, which are repeating sets of three silicate tetrahedra (Figure 1). C-(N-)A-S-H gel is believed to exclude Al-O-Al bonding [32], and to only contain significant Al substitution in the bridging tetrahedral sites defined in Figure 1, not in the paired sites [33]. The mean chain length (MCL) is defined here as the number of silicate and aluminate tetrahedra per C-(N-)A-S-H chain. MCL values for C-(N-)A-S-H gels in alkali-activated slag binders with KOH or NaOH activating solutions have been calculated to be between 4 and 8 [34-37] using a non-crosslinked tobermorite/calcium hydroxide representation of this phase [38], compared with 6-11 for C-(N-)A-S-H gels derived from slag reacted with sodium silicate activators [39].

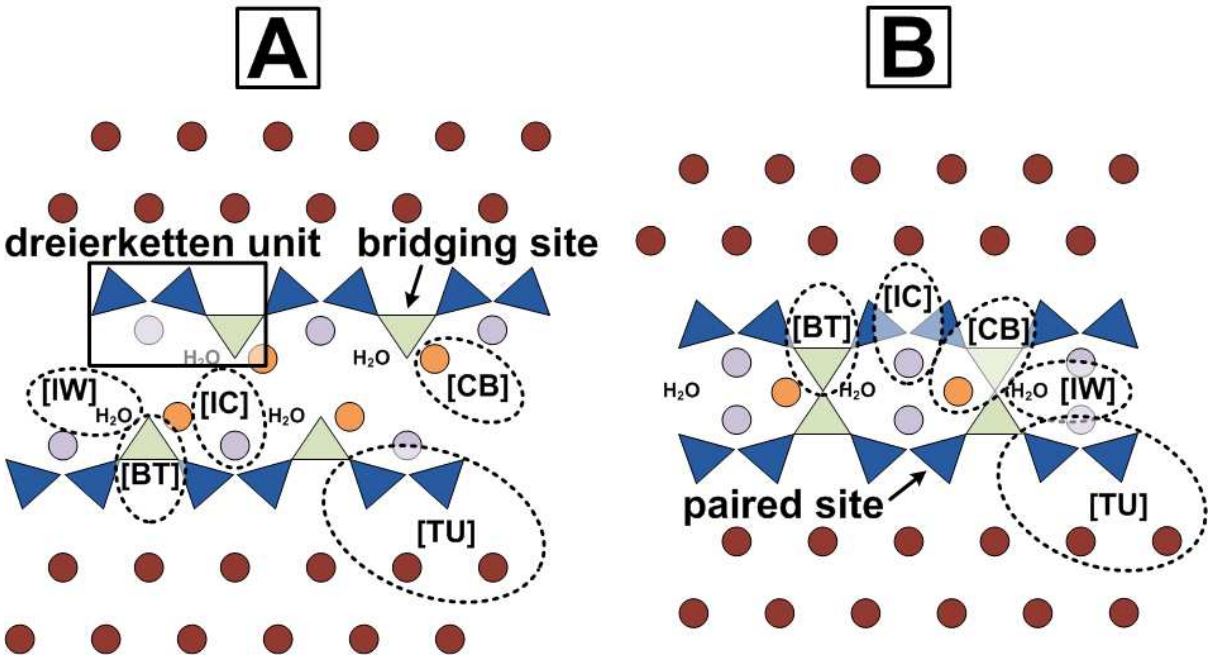

Figure 1. Schematic representations of infinite chain length non-crosslinked (A) and crosslinked (B) C-(N-)A-S-H gel structures, with sublattice sites labelled: *TU*; *BT*; *CB*; *IC*; *IW*, as defined in the text (eqs.(2,4)). Light green and dark blue triangles are paired and bridging tetrahedral sites respectively, dark red circles represent Ca sites in the Ca-O sheets, and the orange and purple circles are positively

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charged species (typically Ca^{2+}, H^+, Na^+ and/or K^+) that charge-balance the aluminosilicate tetrahedra in the BT and TU sites respectively.

Recent experimental results support a partially crosslinked structure for the C-(N-)A-S-H gel formed in Na_2SiO_3-activated slag binders: Q^3 type species have been identified in deconvolutions of ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra in silicate-activated slag cements [39, 40] and in laboratory-synthesised gels [41, 42]. A mixed crosslinked/non-crosslinked structural model was also needed to describe the mechanical properties of hydroxide and silicate-activated slag cements [36].

The majority of AAS and related studies have used GBFS with Al_2O_3 content ≤ 14 wt.% and NaOH, KOH or $Na_2O{\cdot}mSiO_2{\cdot}xH_2O$ activators. Most studies using NaOH or KOH solutions have reported Mg-free binder compositions of 0.7 ≤ Ca/Si ≤ 1.2 and Al/Si ≤ 0.25 [35, 43-45], whereas those derived from $Na_2O{\cdot}mSiO_2{\cdot}xH_2O$ solutions usually report Mg-free binder compositions of 0.6 ≤ Ca/Si ≤ 1.2, Al/Si ≤ 0.25 [39, 40, 45, 46]. Laboratory-synthesised solids containing approximately phase-pure C-(N-)A-S-H gels have typically shown chemical compositions of 0.5 < Ca/(Al+Si) ≤ 1 and Al/Si ≤ 0.20 [42, 47, 48].

Bound water is present in variable amounts in the interlayer spacing in C-S-H type structures, with H_2O/Si ratios between 1.3-1.7 in gels with no adsorbed water [49], and must also be taken into account in development of thermodynamic models for C-(N-)A-S-H gels. The amount of structurally bound water in AAS cement is variable and not yet fully understood [50], so the water contents of 14Å and 11Å tobermorites may also be used to guide the development of thermodynamic models for C-(N-)A-S-H gels. These minerals have bound H_2O/Si ratios of 1.17 and 0.83 respectively [51, 52].

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3. Sublattice solid solution model for C-(N-)A-S-H gel

3.1 Sublattice solid solution definition

There exist several structural models that can describe C-S-H gels, as reviewed in detail by Richardson [53, 54]. However, only the 'Substituted General Model' (SGM) [38] and the 'Crosslinked Substituted Tobermorite Model' (CSTM) [39], can explicitly account for Al-substituted, alkali charge-balanced structures such as C-(N-)A-S-H gel using a fully flexible formulation of the gel chemistry. The CSTM describes C-(N-)A-S-H gel as a mixture of crosslinked and non-crosslinked tobermorite-like structures, and is therefore more generalised than the SGM for systems containing Ca/Si ≤ 1.5 (i.e., excluding solid solution $Ca(OH)_2$). For Ca/Si ≤ 1.5 the treatments of non-crosslinked C-(N-)A-S-H gel components in the SGM and the CSTM are identical, with structural incorporation of Al and charge-balancing by positively-charged interlayer species such as Na^+. These structural models can be used to constrain thermodynamic models because they provide a structurally-consistent basis from which chemical compositions of C-(N-)A-S-H end-members can be determined.

Crosslinked and non-crosslinked C-(N-)A-S-H structures cannot always be distinguished from one another by bulk chemical composition alone, which complicates the ability to differentiate between these two structural types in thermodynamic models for this phase. Therefore, the SGM has been used as a basis from which to derive the chemical composition of the C-(N-)A-S-H gel here explicitly in terms of non-crosslinked structures, without precluding the possibility that the thermodynamic model may also implicitly represent the bulk chemistry of crosslinked C-(N-)A-S-H gels. It is also important to note that the C-S-H gel models derived by Kulik [25] used the 'non-substituted general model' developed by Richardson and Groves [55], which is a simpler model related to the SGM. The notation used by Kulik [25] and Richardson and Groves [38, 55] has been conserved where possible for clarity.

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The SGM can be represented in terms of one dreierketten unit by eq.(1) (details of the derivation up to this point are provided in Appendix A):

$$\left[\mathrm{Ca(OH)_2}\right]_{\left(\frac{u+y-2}{2}\right)}\cdot\left[\left(\mathrm{CaSiO_{3.5}}\right)_2^-\right]\cdot\left[\left(\mathrm{Si}_{(1-a)}R_a\mathrm{O}_2\right)_{(1-\nu)}\right]^{a(1-\nu)-}\cdot\left[\left(l^{c+}_{\frac{a}{c}(1-\nu)}\right)\right]^{a(1-\nu)+}\cdot\left[\mathrm{Ca}_{\left(1-\frac{u}{2}\right)}\mathrm{H}_u\right]^{2+}\cdot h\mathrm{H_2O} \quad (1)$$

where R is a trivalent cation in tetrahedral coordination (e.g. Al^{3+}), l is a charge-balancing interlayer cation (such as Na^+, Ca^{2+} and/or H^+) with a positive charge of c, a is the extent of R substitution in bridging sites (Figure 1), v is the fraction of bridging site vacancies per dreierketten unit, u is the interlayer H^+ content per dreierketten unit for the main chain sites (TU, $\mathrm{CaSiO_{3.5}^-}$), and h defines the amount of water per dreierketten unit. The SGM explicitly defines Al substitution in bridging sites only, and excludes Al-O-Al bonding, consistent with Loewenstein's rule [32].

Eq.(1) can be equivalently written in sublattice notation as eq.(2):

$$\left[CU\right]_2\cdot\left[TU^-\right]_2\cdot\left[BT^{a(1-\nu)-}\right]_1\cdot\left[CB^{a(1-\nu)+}\right]_1\cdot\left[IC^{2+}\right]_1\cdot\left[IW\right]_h \quad (2)$$

where CU represents interstitial 'solid solution' $Ca(OH)_2$ [55], BT are the bridging tetrahedra ($Si_{(1-a)}R_aO_{2(1-v)}^{a(1-v)-}$), CB are the interlayer charge-balancing species for the bridging tetrahedra ($l_{a(1-v)/c}^{a(1-v)+}$), IC are the interlayer charge-balancing species for the TU sites ($Ca_{(1-u/2)}H_u^{2+}$), and IW represents interlayer water (H_2O). The CU sites in tobermorite are vacant (there is no interstitial 'solid solution' $Ca(OH)_2$), and are therefore eliminated from the structural definition in eqs.(1-2). This limits the chemical composition of the sublattice solid solution model to $0.67 \le Ca/Si \le 1.5$ and leads to eqs.(3-4):

$$\left[\left(\mathrm{CaSiO_{3.5}}\right)_2^-\right]\cdot\left[\left(\mathrm{Si}_{(1-a)}R_a\mathrm{O}_2\right)_{(1-\nu)}\right]^{a(1-\nu)-}\cdot\left[\left(l^{c+}_{\frac{a}{c}(1-\nu)}\right)\right]^{a(1-\nu)+}\cdot\left[\mathrm{Ca}_{\left(1-\frac{u}{2}\right)}\mathrm{H}_u\right]^{2+}\cdot h\mathrm{H_2O} \quad (3)$$

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$$\left[TU^{-}\right]_2 \cdot \left[BT^{a(1-\nu)-}\right]_1 \cdot \left[CB^{a(1-\nu)+}\right]_1 \cdot \left[IC^{2+}\right]_1 \cdot \left[IW\right]_h \quad (4)$$

This elimination of $Ca(OH)_2$ therefore provides the major limitation on the domain of applicability of the model described here; it is not able to be used for Ca/Si ratios > 1.5, but is valuable for alkali-activated cements and blended PC/SCM materials in which the composition of the C-(N-)A-S-H gel formed falls below this ratio. The sublattice sites shown in eq.(4) are illustrated in Figure 1.

The IC sites are now modified to enable the TU sites to be charge-balanced by Na^+ species in addition to the BT sites. The possible interlayer charge-balancing species in C-(N-)A-S-H gel are not limited to Ca^{2+}, H^+ and Na^+, but these are the only species for which sufficient data have been published to enable validation of the thermodynamic model developed here. Na-based solutions are also the most relevant alkaline activators for commercial use because they are relatively inexpensive and widely available [29]. The BT sites in C-(N-)A-S-H gel are mostly filled by vacancies, Si and/or Al species, meaning that R = Al can also be specified. Eq.(3) is re-written with the modified IC sites and with similarly modified CB sites, and with Al-substitution in the BT sites, which results in eq.(5):

$$\left[\left(CaSiO_{3.5}\right)_2^-\right] \cdot \left[\left(Si_{(1-a)}Al_aO_2\right)_{(1-\nu)}\right]^{a(1-\nu)-} \cdot \left[\left(Ca_{\left(\frac{1-d_1-d_2}{2}\right)}H_{d_1}Na_{d_2}\right)_{a(1-\nu)}\right]^{a(1-\nu)+} \cdot \left[Ca_{\left(\frac{2-e_1-e_2}{2}\right)}H_{e_1}Na_{e_2}\right]^{2+} \cdot hH_2O \quad (5)$$

where $d_1 + d_2 \leq 1$ and $e_1 + e_2 \leq 2$.

While eqs.(4-5) are satisfactory for thermodynamic modelling, it is desirable to obtain a thermodynamic model which is consistent with existing validated formulations such as the downscaled CSH3T model [25]. In that model, the BT, CB and IC sites are combined into two potentially-equivalent BCI sites that could have different substitutions via the choice of two sublattice species, and the sublattice formula was 'downscaled' to 0.5 dreierketten units. The use of two such sites, rather than a single BCI site, is beneficial because it increases the number of unique chemical compositions that can be represented by the sublattice solid solution and can greatly

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206 improve the fit of the thermodynamic model output to the validation data (e.g. solubility
207 measurements) for the same set of mixing rules used (e.g. simple random ideal mixing). However,
208 this means that end-member stoichiometries, and sublattice species and formulae are more likely to
209 be represented in terms of fractional quantities rather than integer amounts. Fractional expressions
210 obviously cannot directly correspond to atomistic-level structures, which means that
211 thermodynamic models developed in this way can only describe the chemistry of solid solutions on
212 the bulk scale rather than at the atomistic scale. Therefore, downscaling is useful in the
213 development of thermodynamic models to describe complex phases such as C-(N-)A-S-H gels with
214 atomistic structures that have not yet been fully resolved. Here, downscaling is essential to improve
215 the number of unique chemical compositions and the volume of experimental data described by the
216 sublattice solid solution model while keeping its formulation relatively simple, particularly because
217 this model is required to describe C-(N-)A-S-H gel chemistry in the complex AAS cement system. The
218 downscaled chemical and sublattice formulae (to 0.5 dreierketten units), written in terms of
219 potentially-equivalent BCI sites ($BCI = BT + CB + IC$) and thus consistent with the downscaled
220 CSH3T model [25], are shown in eqs.(6-7) respectively:

221 $$\left[\mathrm{CaSiO_{3.5}}\right]^{-} \cdot \left[\left\{ \left(\mathrm{Si_{(1-a)}Al_aO_2}\right)_{\frac{(1-\nu)}{2}} \cdot \left(\mathrm{Ca_{\left(\frac{1-d_1-d_2}{2}\right)}H_{d_1}Na_{d_2}}\right)_{\frac{a(1-\nu)}{2}} \cdot \left(\mathrm{Ca_{\left(\frac{2-e_1-e_2}{2}\right)}H_{e_1}Na_{e_2}}\right)_{\frac{1}{2}} \right\}_{\frac{1}{2}}^{0.5+} \right]_2 \cdot \left[\left(\frac{h}{2}\right)\mathrm{H_2O}\right]$$

222 (6)

223 $$\left[TU^{-}\right]_1 \cdot \left[BCI^{0.5+}\right]_1 \cdot \left[BCI^{0.5+}\right]_1 \cdot \left[IW\right]_{\frac{h}{2}} \quad (7)$$

224

225 Here, at least one additional (Al,Na)-containing sublattice species is necessary to represent C-(N-)A-
226 S-H gel chemistry, compared to previous thermodynamic models for the CaO-SiO_2-H_2O system.
227 Increasing the number of sublattice species and sites allows the description of a greater diversity of
228 bulk C-(N-)A-S-H gel chemical compositions, and facilitates independent incorporation of Na and Al
229 in C-S-H type structures. Additionally, as the quantities of bound water in C-(N-)A-S-H and C-S-H gels

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are significantly different [50, 56], it is also necessary to allow for variation in the IW site. Here, C-(N-)A-S-H gels are assumed to contain one mole of H_2O in the IW site per 0.5 dreierketten units (h = 2), because this is approximately equal to the chemistry of 11 Å and 14 Å tobermorites [51, 52] and the C-A-S-H type gels formed in AAS binders ($H_2O/Si \approx 1$) [50].

These factors thus require the use of a sixth-order sublattice solid solution for the C-(N-)A-S-H thermodynamic model developed here. This solid solution contains five BCI sites, with each carrying a positive charge of 0.125 and grouped as shown in eqs.(8-9), and one variable IW site:

$$\left[\mathrm{CaSiO_{3.5}}\right]^{-}\cdot\left[\mathrm{H_2O}\right]\cdot\left[\left\{\left(\mathrm{Si_{(1-a)}Al_aO_2}\right)_{\frac{(1-\nu)}{2}}\cdot\left(\mathrm{Ca_{\left(\frac{1-d_1-d_2}{2}\right)}H_{d_1}Na_{d_2}}\right)_{\frac{a(1-\nu)}{2}}\cdot\left(\mathrm{Ca_{\left(\frac{2-e_1-e_2}{2}\right)}H_{e_1}Na_{e_2}}\right)_{\frac{1}{2}}\right\}_{\frac{1}{8}}^{0.125+}\right]_8\cdot\left[\left(\frac{h}{2}-1\right)\mathrm{H_2O}\right] \quad (8)$$

$$\left[TU^{-}\right]_1\cdot\left[IW*\right]_1\cdot\left[BCI^{0.125+}\right]_2\cdot\left[BCI^{0.125+}\right]_2\cdot\left[BCI^{0.125+}\right]_2\cdot\left[BCI^{0.125+}\right]_1\cdot\left[BCI^{0.125+}\right]_1\cdot\left[IW\right]_1 \quad (9)$$

where IW* represents a fixed interlayer water site (with full occupancy of H_2O but otherwise identical to the IW site depicted in Figure 1). Eqs.(8-9) are the fundamental formulae that represent the C-(N-)A-S-H thermodynamic model developed here.

3.2 End-member selection

As discussed in section 1, a goal of this study is to develop a sublattice solid solution model that can describe the solubility and chemical composition of C-(N-)A-S-H gel in AAS cements. Based on the sublattice solid solution definition established in eqs.(8-9), it is now necessary to select a set of end-members, sublattice sites and species that can represent the chemistry of C-(N-)A-S-H gel.

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Six species that can substitute into the five *BCI* sites given in eq.(9), and which are compatible with the chemical formula for these sites (eq.(8)) and the chemistry of C-(N-)A-S-H gels in AAS cements, were selected to represent a sublattice solid solution of the form shown in eq.(10):

$$Q^{*}\left[A,B,C,D,E\right]_{\mathrm{I}}^{n_1}\left[F,G,H,I,J\right]_{\mathrm{II}}^{n_2}\left[K,L,M\right]_{\mathrm{III}}^{n_3}\left[N,O,P,Q,R,S\right]_{\mathrm{IV}}^{n_4}\left[T,U,V,W\right]_{\mathrm{V}}^{n_5}\left[X,Y\right]_{\mathrm{VI}}^{n_6} \quad (10)$$

Here, species A,F,K,N,T are $Ca_{0.0625}O_{0.0625}H_{0.125}^{0.125+}$, B,G,L,O,U are $Si_{0.0625}O_{0.125}H_{0.125}^{0.125+}$ and D,I,M,Q,V are $Si_{0.0625}O_{0.125}Na_{0.125}^{0.125+}$, which can be present in five different *BCI* sites, the species C,H,P are $Al_{0.0625}O_{0.125}H_{0.1875}^{0.125+}$ and E,J,R are $Al_{0.0625}Na_{0.0625}O_{0.125}H_{0.125}^{0.125+}$, which can fill four of the *BCI* sites, the species S,W are $Ca_{0.0625}O_{0.0625}Na_{0.125}^{0.125+}$, which can fill two of the *BCI* sites, X is H_2O, Y is a vacancy (V_{IW}), and Q^{*} is $CaSiO_{3.5}^{-}\cdot H_2O$. This combination of sublattice sites and species was chosen as it comprises the least complex formulation of the sublattice solid solution that can represent the chemistry of the C-(N-)A-S-H gel in AAS cements. In this work the coefficients $\mathrm{I}=2$, $\mathrm{II}=2$, $\mathrm{III}=2$, $\mathrm{IV}=1$, $\mathrm{V}=1$ and $\mathrm{VI}=1$ define the stoichiometry of the sublattice sites, and the superscripts n_1, n_2, n_3, n_4, n_5 and n_6 correspond to the five *BCI* sites and single *IW* site in eq.(9). Vacancies in *BCI* sites are included in the thermodynamic model via the v parameter in eq.(8).

A minimal set of eight end-members was chosen within this sublattice solid solution model to define the C-(N-)A-S-H gel in this work, as shown in Table 1. This is the smallest number of end-members that can resemble the chemistry of C-(N-)A-S-H gels (section 2) and describe the available solubility data for AAS cement and the CaO-(Na_2O,Al_2O_3)-SiO_2-H_2O systems (section 6). The solid solution contains three C-S-H end-members, one C-(N-)S-H end-member, two C-A-S-H end-members and two C-(N-)A-S-H end-members. The C-S-H end-members have the same chemical compositions as the T2C, T5C and TobH end-members of the downscaled CSH3T model (T2C*, T5C* and TobH* respectively) [25], which contain the *TU* site, $h = 4$, and two *BCI* sublattice species, $Si_{0.25}O_{0.5}H_{0.5}^{+}$ and $Ca_{0.25}O_{0.25}H_{0.5}^{+}$, for $a = 0$, to cover the range 0.67 ≤ Ca/Si ≤ 1.5 in the CaO-SiO_2-H_2O system. One

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278 H_2O molecule is also added per vacancy in the bridging tetrahedra for each of the eight end-

279 members (determined by the value of v).

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Table 1. Chemical compositions of the eight end-members of the C-(N-)A-S-H thermodynamic model, and parameters chosen for use in eq.(8). One H_2O molecule is added to the *BCI* site per bridging site vacancy for consistency with the C-S-H thermodynamic model developed by Kulik [25].

End-member	v	a	i_1	i_2	u_1	u_2	M	Sublattice formula [b]	Chemical formula
5CA	0.5	1	1	0	1	0	2	$[(CaSiO_{3.5})^-]_1{\cdot}[H_2O]_1{\cdot}[Al_{0.0625}O_{0.125}H_{0.1875}{}^{0.125+}]_2{\cdot}$ $[Al_{0.0625}O_{0.125}H_{0.1875}{}^{0.125+}]_2{\cdot}[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_1{\cdot}[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_1{\cdot}[V_{H2O}]_1$	$(CaO)_{1.25}(Al_2O_3)_{0.125}(SiO_2)_1(H_2O)_{1.625}$
INFCA	0	0.625	1	0	2	0	2	$[(CaSiO_{3.5})^-]_1{\cdot}[H_2O]_1{\cdot}[Al_{0.0625}O_{0.125}H_{0.1875}{}^{0.125+}]_2{\cdot}$ $[Al_{0.0625}O_{0.125}H_{0.1875}{}^{0.125+}]_2{\cdot}[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Al_{0.0625}O_{0.125}H_{0.1875}{}^{0.125+}]_1{\cdot}[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_1{\cdot}[V_{H2O}]_1$	$(CaO)_1(Al_2O_3)_{0.15625}(SiO_2)_{1.1875}(H_2O)_{1.65625}$
5CNA	0.5	1	0	1	0.5	0.5	2	$[(CaSiO_{3.5})^-]_1{\cdot}[H_2O]_1{\cdot}[Al_{0.0625}Na_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Al_{0.0625}Na_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Ca_{0.0625}O_{0.0625}Na_{0.125}{}^{0.125+}]_1{\cdot}[Ca_{0.0625}O_{0.0625}Na_{0.125}{}^{0.125+}]_1{\cdot}[V_{H2O}]_1$	$(CaO)_{1.25}(Na_2O)_{0.25}(Al_2O_3)_{0.125}(SiO_2)_1(H_2O)_{1.375}$
INFCNA	0	0.625	0	1	1.25	0.75	2	$[(CaSiO_{3.5})^-]_1{\cdot}[H_2O]_1{\cdot}[Al_{0.0625}Na_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Al_{0.0625}Na_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}[Si_{0.0625}O_{0.125}Na_{0.125}{}^{0.125+}]_2{\cdot}$ $[Al_{0.0625}Na_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_1{\cdot}[Si_{0.0625}O_{0.125}Na_{0.125}{}^{0.125+}]_1{\cdot}[V_{H2O}]_1$	$(CaO)_1(Na_2O)_{0.34375}(Al_2O_3)_{0.15625}(SiO_2)_{1.1875}(H_2O)_{1.3125}$
INFCN	0	0	1	0	0.75	1.25	2	$[(CaSiO_{3.5})^-]_1{\cdot}[H_2O]_1{\cdot}[Si_{0.0625}O_{0.125}Na_{0.125}{}^{0.125+}]_2{\cdot}$ $[Si_{0.0625}O_{0.125}Na_{0.125}{}^{0.125+}]_2{\cdot}[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Si_{0.0625}O_{0.125}Na_{0.125}{}^{0.125+}]_1{\cdot}[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_1{\cdot}[V_{H2O}]_1$	$(CaO)_1(Na_2O)_{0.3125}(SiO_2)_{1.5}(H_2O)_{1.1875}$
T2C* [a]	1	0	0	0	0	0	4	$[(CaSiO_{3.5})^-]_1{\cdot}[H_2O]_1{\cdot}[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_2{\cdot}[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_1{\cdot}[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_1{\cdot}[H_2O]_1$	$(CaO)_{1.5}(SiO_2)_1(H_2O)_{2.5}$
T5C* [a]	0.5	0	0	0	1	0	4	$[(CaSiO_{3.5})^-]_1{\cdot}[H_2O]_1{\cdot}[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_1{\cdot}[Ca_{0.0625}O_{0.0625}H_{0.125}{}^{0.125+}]_1{\cdot}[H_2O]_1$	$(CaO)_{1.25}(SiO_2)_{1.25}(H_2O)_{2.5}$
TobH* [a]	0	0	0	0	2	0	4	$[(CaSiO_{3.5})^-]_1{\cdot}[H_2O]_1{\cdot}[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_2{\cdot}$ $[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_1{\cdot}[Si_{0.0625}O_{0.125}H_{0.125}{}^{0.125+}]_1{\cdot}[H_2O]_1$	$(CaO)_1(SiO_2)_{1.5}(H_2O)_{2.5}$

[a] The asterisks for the T2C*, T5C* and TobH* end-members indicate that these components have the same bulk chemistry but slightly modified thermodynamic properties relative to the T2C, T5C and TobH end-members of the downscaled CSH3T model [25].

[b] V_{H2O} is a vacancy in the *IW* sublattice site.

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As each species (A to Y) is defined to only substitute into one site (i.e., species with the same chemistry but occupying different sites are treated as being distinct), the site fraction of a species i in a given site n_s, $y_i^{n_s}$, is defined as $y_i^{n_s} = \sum\left(\chi_k^{i,n_s}\right)$ for $\sum\left(y_i^{n_s}\right)=1$. Here $n_s \in \{n_1, n_2, n_3, n_4, n_5, n_6\}$ is the sublattice site, χ_k^{i,n_s} is the effective mole fraction of end-member k containing the species i in the sublattice site n_s, with $\sum_k\left(\chi_k\right)=1$. In defining an end-member of the sublattice solid solution model, the species present in the s^{th} sublattice site may be identified by the same subscript number i.e. i_1 is the species present in the sublattice site n_1, and $i_1 \in \{A, B, C, D, E\}$. Thus an end-member can be equivalently written in terms of its substituting species, i.e. $k = i_1 i_2 i_3 \cdots i_s$.

The chain length (CL) for each of the end-members, and the MCL of the C-(N-)A-S-H gel as a whole, can then be calculated from eq.(11).

$$CL = \frac{3}{\sum_k\left(\chi_k \nu_k\right)} - 1 \tag{11}$$

The fraction of bridging site vacancies per dreierketten unit, ν, is shown in Table 1 for each end-member of the C-(N-)A-S-H thermodynamic model. This equation represents the minimum chain length possible for the end-members, and thus the minimum MCL of the C-(N-)A-S-H gel, because eq.(11) implies that the end-members are strictly non-crosslinked. The chain lengths of crosslinked C-(N-)A-S-H end-members would be calculated in the same way, but with a factor of two included (i.e. $CL_{crosslinked} = 2CL$) to reflect the double chain structures in these phases. Here, these crosslinked and non-crosslinked structures were not explicitly differentiated in defining the end-members (eqs.(8-9)), meaning that eq.(11) provides a lower bound on the MCLs of partially (or fully) crosslinked C-(N-)A-S-H gels.

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4. Thermodynamic basis of the sublattice solid solution model

The chemical potential (partial molal Gibbs free energy), $\mu_{i_1 i_2 i_3 \cdots i_s}$, of end-member $i_1 i_2 i_3 \cdots i_s$ in a multi-component solid solution can be represented by eq.(12) [57]:

$$\mu_{i_1 i_2 i_3 \cdots i_s} = G_m + \left[\frac{\partial G_m}{\partial y_{i_1}^{n_1}} + \frac{\partial G_m}{\partial y_{i_2}^{n_2}} + \frac{\partial G_m}{\partial y_{i_3}^{n_3}} + \cdots + \frac{\partial G_m}{\partial y_{i_s}^{n_s}} \right] - \left[\sum_i \left(y_i \frac{\partial G_m}{\partial y_i} \right) \right] \quad (12)$$

where G_m is the Gibbs free energy of mixing using the notation previously introduced, and can be expressed by eq.(13) [58]:

$$G_m = G^{mech} - TS_m^{id} + G_m^E \quad (13)$$

where G^{mech} is the Gibbs free energy of a compositionally-equivalent 'mechanical mixture' of simple components to the solid solution phase, $S_m{}^{id}$ is the difference in entropy between the ideal solid solution for the solid phase and its end-member components (i.e. the configurational entropy), and $G_m{}^E$ is the excess Gibbs free energy of mixing (representing the deviation of the solid solution from ideality).

Here, the 'compound energy formalism' is used to define the surface of reference for the Gibbs free energy of mixing as a weighted average of the Gibbs free energy of each of the (pure) end-members in the C-(N-)A-S-H solid solution [57]. This is formally expressed by eq.(14) for a multi-site, multi-component sublattice solid solution, assuming random mixing within each sublattice [59]:

$$G_m = \left[\sum_{n_1} \sum_{n_2} \sum_{n_3} \cdots \sum_{n_s} \left(y_{i_1}^{n_1} y_{i_2}^{n_2} y_{i_3}^{n_3} \cdots y_{i_s}^{n_s} \right) \; {}^{o}G_{i_1 i_2 i_3 \cdots i_s} \right] + R^* T \left[\mathrm{I} \sum_{i_1} \left(y_{i_1} \ln y_{i_1} \right) + \mathrm{II} \sum_{i_2} \left(y_{i_2} \ln y_{i_2} \right) + \mathrm{III} \sum_{i_3} \left(y_{i_3} \ln y_{i_3} \right) + \cdots + \zeta \sum_{i_s} \left(y_{i_s} \ln y_{i_s} \right) \right] + G_m^E \quad (14)$$

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where ${}^{o}G_{i_1 i_2 i_3 \cdots i_s}$ is the standard Gibbs free energy of end-member $i_1 i_2 i_3 \cdots i_s$, R^* is the universal gas constant, T is temperature and ζ is the stoichiometric coefficient of the s^{th} sublattice site. The random mixing assumption is appropriate here because it greatly simplifies the expression for the configurational entropy and because the solid solution definition (eqs.(8-9)) does not represent atomic-scale structures; assigning hypothetical weightings to non-physical mixing combinations would not make physical sense. This choice is reasonable given that this is the first attempt to develop a sublattice solid solution model for C-(N-)A-S-H gel, and will be validated in section 6 through the ability of the model to accurately describe chemical composition and solubility data for this phase.

Eq.(14) can be expanded explicitly for the sublattice solid solution defined by the eight end-members shown in Table 1. Substituting this expanded version of eq.(14) into eq.(12), defining a generalised end-member with species A, F, K, N, T, X in sublattice sites n_1, n_2, n_3, n_4, n_5, n_6 and then simplifying, results in eq.(15):

$$\mu_{AFKNTX} = {}^{o}G_{AFKNTX} + RT\left[2\ln\left(y_A\right) + 2\ln\left(y_F\right) + 2\ln\left(y_K\right) + \ln\left(y_N\right) + \ln\left(y_T\right) + \ln\left(y_X\right)\right] + G_m^E + U \quad (15)$$

Equivalent relationships for μ_{AFKNTX} can be written for all other combinations of sublattice site occupancies. The U term contains the Gibbs free energies for the reciprocal reactions ($\Delta_{rcp}{}^{o}G$), which denotes the difference in Gibbs free energy between combinations of end-members in the sublattice solid solution (which must by definition contain equal numbers of reactant and product terms). For example, the reciprocal reaction (eq.(16)) has a corresponding Gibbs free energy of reaction given by eq.(17):

$$AFKOTX + AFLNTX \leftrightarrow AFKNTX + AFLOTX \quad (16)$$

$$\Delta_{rcp}{}^{o}G_{LO} = {}^{o}G_{AFKOTX} + {}^{o}G_{AFLNTX} - {}^{o}G_{AFKNTX} - {}^{o}G_{AFLOTX} \quad (17)$$

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It is possible to make two key simplifications here. The first is setting G_m^E = 0, i.e. interactions between atoms in the same sublattice sites are neglected, meaning that the sublattice solid solution model is ideal. The second is that the Gibbs free energies of the reciprocal reactions in the solid solution are numerically approximated to zero (U = 0). The reciprocal reaction terms describe the nearest-neighbour interactions in the solid solution, so are likely to influence end-member chemical potentials more than the next-nearest-neighbour interactions described by the excess Gibbs free energy terms. These terms are likely to be non-zero in C-(N-)A-S-H gels, because it is known that thermodynamic energetic differences arise from nearest-neighbour Si-Al substitution in aluminosilicate systems [60], but this approach can be validated by the good fit of the thermodynamic model to the published solubility and chemical composition data in the CaO-(Na_2O,Al_2O_3)-SiO_2-H_2O systems (section 6). In defining the mixing rules in this way, the accuracy of the thermodynamic model is determined semi-empirically through the use of end-members with carefully selected chemical compositions and Gibbs free energies that internalise the nearest and next-nearest neighbour interactions in C-(N-)A-S-H gels, rather than through the explicit definition of these interactions. However, quantification of these interactions in terms of chemical potentials for hypothetical C-(N-)A-S-H end-members, and a better understanding of the solubility of C-(N-)A-S-H gels, will be important future steps in the model development.

Application of these assumptions to eq.(15) leads to the final, simplified formula for the chemical potential of an end-member in the C-(N-)A-S-H sublattice solid solution model (eq.(18)):

$$\mu_{AFKNTX} = {}^{o}G_{AFKNTX} + RT\left[2\ln\left(y_A\right)+2\ln\left(y_F\right)+2\ln\left(y_K\right)+\ln\left(y_N\right)+\ln\left(y_T\right)+\ln\left(y_X\right)\right] \quad (18)$$

The C-(N-)A-S-H thermodynamic model developed here is implemented in the GEM-Selektor v3 thermodynamic modelling software (http://gems.web.psi.ch/) [61, 62]. Sublattice solid solution models can be specified in GEM-Selektor by modifying the activities of the chosen end-members

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(Table 1) through the introduction of a 'fictive activity coefficient' λ, which internalises the thermodynamic mixing relationships within the solid solution. This method was used in the C-S-H thermodynamic model developed by Kulik [25]. The fictive activity coefficient is defined by eq.(19):

$$\lambda_k = \frac{\alpha_k}{\chi_k} \tag{19}$$

where α_k is the activity of the k^{th} end-member, eq.(20):

$$\mu_k = \mu_k^o + RT\ln(\alpha_k) \tag{20}$$

The fictive activity coefficient is defined by eliminating μ_k and the ${}^oG_{AFKNTX}$ term (equivalent to $\mu_k{}^o$ as defined here) from eqs.(18,20), then substituting eq.(19) into the resulting equation and simplifying to obtain eq.(21):

$$\ln(\lambda_{AFKNTX}) = \left[2\ln(y_A) + 2\ln(y_F) + 2\ln(y_K) + \ln(y_N) + \ln(y_T) + \ln(y_X)\right] - \ln(\chi_{AFKNTX}) \tag{21}$$

Relationships equivalent to eq.(21) can thus be obtained for all eight end-members (Table 1). The fictive activity coefficient relationships for these end-members are shown in Appendix B.

5. Modelling method

5.1 Modelling system definition

The kernel Nagra/PSI [63], which is the default thermodynamic database for GEM-Selektor v3 (http://gems.web.psi.ch/) [61, 62], and the CEMDATA07 thermodynamic database [17, 23, 64-69], which contains data for various compounds commonly found in cement systems, were used during simulations. The ideal gas equation of state is used to describe the gases and the Truesdell-Jones form of the extended Debye-Hückel equation, eq.(22) [70], is used to describe the aqueous species.

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$$\log_{10}\gamma_j = \frac{-A_\gamma z_j^2\sqrt{I}}{1+\dot{a}B_\gamma\sqrt{I}} + b_\gamma I + \log_{10}\frac{x_{jw}}{X_w} \quad (22)$$

Here, γ_j and z_j are the activity coefficient and charge of the j^{th} aqueous species respectively, A_γ and B_γ are temperature and pressure-dependent electrostatic parameters, I is the ionic strength of the aqueous electrolyte phase, $\dot{a}$ is the ion size parameter, b_γ is a parameter that describes short-range interactions between charged aqueous species in an electrolyte solution (representing the predominant electrolyte in the system), x_{jw} is the molar quantity of water, and X_w is the total molar amount of the aqueous phase. Constant values of $\dot{a}$ (3.31 Å) and b_γ (0.098 kg/mol) are taken to represent the average ion size and common short-range interactions of charged aqueous species in a NaOH-dominated solution [70]. The water activity is calculated from the osmotic coefficient [70].

The extended Debye-Hückel equation is accurate at moderate ionic strengths (up to ~ 1 molal) [70], which is lower than the ionic strength in AAS pore solutions (~1-3 molal in sodium silicate activated slag cements, e.g. [71]), but this equation was chosen here as a first step in development of the thermodynamic model as it is directly encoded in GEM-Selektor. Additionally, the description of aqueous silicate speciation in the GEM-Selektor databases does not currently extend beyond dimeric silicate and aluminosilicate units, and adsorption of aqueous species onto simulated solid phases is also not fully taken into account. Use of an improved aqueous phase model, such as the Pitzer model [72] coupled with a more complete description of silicate oligomerisation [73], and description of sorption effects, are goals of future work.

5.2 Thermodynamic property estimation

The standard absolute isobaric heat capacity (Cp^o) and absolute entropy at standard state (S^o) of the five (Al,Na)-containing C-(N-)A-S-H end-members were estimated using the additivity method and eq.(23), defined in terms of structurally-relevant constituents: T2C (the Ca-rich end-member of the

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downscaled CSH3T model [25], $(CaO)_{1.5}(SiO_2)_1(H_2O)_{2.5}$, portlandite ($Ca(OH)_2$), amorphous SiO_2, gibbsite ($Al(OH)_3$) and NaOH $_{(s)}$.

$$\begin{aligned}\Phi^o_{(CaO)_{a'}(SiO_2)_{b'}(Al_2O_3)_{c'}(Na_2O)_{d'}(H_2O)_{e'}} &= \frac{1}{2}(5a'-3e'+9c'+3d')\Phi^o_{Ca(OH)_2} \\ &+(b'-e'+a'+3c'+d)\Phi^o_{SiO_2}+2c'\Phi^o_{Al(OH)_3}+2d'\Phi^o_{NaOH} \\ &+(e'-a'-3c'-d')\Phi^o_{(CaO)_{1.5}(SiO_2)_1(H_2O)_{2.5}}\end{aligned} \quad (23)$$

Here Φ^o denotes the standard thermodynamic property undergoing estimation (Cp^o or S^o), *a'*, *b'*, *c'*, *d'*, *e'* are the stoichiometric coefficients for the respective oxide components CaO, SiO_2, Al_2O_3, Na_2O and H_2O, and the numerical coefficients for these terms are the values that result from solving the elemental balance for eq.(23). The thermodynamic properties of the constituent phases are provided in Appendix C, and are consistent with the Nagra/PSI [63] and CEMDATA07 thermodynamic databases [17, 23, 64-69]. The additivity method is expected to yield relatively small errors in estimated values for Cp^o and S^o if suitable constituents are chosen [74]. The changes in S^o and Cp^o, and the solubility product (K_{so}) of the (Al,Na)-containing C-(N-)A-S-H end-members for the dissociation reaction represented by eq.(24), were determined to enable thermodynamic property calculations in GEM-Selektor:

$$\begin{aligned}(CaO)_{a'}(SiO_2)_{b'}(Al_2O_3)_{c'}(Na_2O)_{d'}(H_2O)_{e'(s)} &\xleftrightarrow{K_{so}} a'Ca^{2+}_{(aq)} \\ &+b'SiO_3^{2-}{}_{(aq)}+2c'AlO_2^{-}{}_{(aq)}+2d'Na^{+}_{(aq)}+2(a'-b'-c'+d')OH^{-}_{(aq)} \\ &+(b'+c'+e'-a'-d')H_2O_{(l)}\end{aligned} \quad (24)$$

The ReacDC module in GEM-Selektor was used to determine the standard partial molal Gibbs free energies ($\Delta_f G^o$) and enthalpies of formation ($\Delta_f H^o$) for the proposed C-(N-)A-S-H end-members by specifying 'optimised' solubility products for the reaction shown in eq.(24), the value of S^o determined via the additivity method (using the components listed previously), and the change in S^o of the dissociation reaction (eq.(24)). The Gibbs free energies (and thus the enthalpies) of the T2C*,

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448 T5C* and TobH* end-members were modified slightly from the values reported in the downscaled
449 CSH3T model [25], and solubility products of the (Al,Na)-containing C-(N-)A-S-H end-members were
450 selected, to obtain the optimised fit of the thermodynamic model to the solubility and solid phase
451 chemistry data in the CaO-(Na_2O,Al_2O_3)-SiO_2-H_2O [2-15, 41, 42, 48, 75-81] and AAS cement systems
452 [71, 82-84] used in model validation (section 6). All other thermodynamic parameters of the T2C*,
453 T5C* and TobH* end-members were adopted directly from the downscaled CSH3T model.

454

455 Standard molar volumes (V^o) of the (Al,Na)-containing C-(N-)A-S-H end-members were determined
456 from density calculations using the method proposed by Thomas et al. [50], but extended to include
457 Na species via eq.(25):

458 $$\rho^{sc}{}_{CNASH} = N_A \rho'_{CNASH} \left[\frac{\left(\frac{CaO}{SiO_2}\right) b^{sc}{}_{CaO} + b^{sc}{}_{SiO_2} + \left(\frac{Al_2O_3}{SiO_2}\right) b^{sc}{}_{Al_2O_3} + \left(\frac{Na_2O}{SiO_2}\right) b^{sc}{}_{Na_2O} + \left(\frac{H_2O}{SiO_2}\right) b^{sc}{}_{H_2O}}{MW_{CNASH}} \right] \quad (25)$$

459 where the b^{sc} parameters are the established neutron scattering lengths for CaO, SiO_2, Al_2O_3, Na_2O
460 and H_2O, ρ^{sc} is the scattering length density taken from the literature [50], ρ'_{CNASH} is the predicted
461 density of a C-(N-)A-S-H end-member, N_A is Avogadro's number, MW_{CNASH} is the molecular weight of
462 a C-(N-)A-S-H end-member, and the ratios CaO/SiO_2, Al_2O_3/SiO_2, Na_2O/SiO_2, and H_2O/SiO_2 are molar
463 composition ratios of a C-(N-)A-S-H end-member. The optimised thermodynamic properties for the
464 C-(N-)A-S-H end-members are summarised in Table 2.

465

466 **Table 2**. Thermodynamic properties, densities and the change in thermodynamic properties for the
467 dissociation reaction (eq.(24)) for the end-members of the C-(N-)A-S-H solid solution (25°C, 1 bar)

	Standard thermodynamic properties and density					
End-member	$V°$ (cm³/mol)	$\Delta_f H°$ (kJ/mol)	$\Delta_f G°$ (kJ/mol)	$S°$ (J/mol.K)	$Cp°$ (J/mol.K)	ρ'_{CNASH} (g/cm³)
5CA	57.3	-2491	-2293	163	177	3.01
INFCA	59.3	-2551	-2343	154	181	2.92
5CNA	64.5	-2569	-2382	195	176	2.84
INFCNA	69.3	-2667	-2474	198	180	2.72
INFCN	71.1	-2642	-2452	186	184	2.63
T2C* [a]	80.6	-2721	-2465	167	237	2.35
T5C* [a]	79.3	-2780	-2517	160	234	2.40

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TobH* [a]	85.0	-2831	-2560	153	231	2.25

Change in thermodynamic properties for the dissociation reaction (eq.(24))

End-member	$\Delta_r V°$ (cm³/mol)	$\Delta_r H°$ (kJ/mol)	$\Delta_r G°$ (kJ/mol)	$\Delta_r S°$ (J/mol.K)	$\Delta_r Cp°$ (J/mol.K)	$\log_{10}(K_{so})$
5CA	-17.9	-4.0	61.4	-219	-29.3	-10.75
INFCA	5.1	0.58	50.8	-168	160	-8.90
5CNA	-37.1	-18.8	59.4	-262	-115	-10.4
INFCNA	-21.3	-10.8	57.1	-228	41.5	-10.0
INFCN	-12.5	-6.2	61.1	-226	144	-10.7

[a] The $\log_{10}(K_{so})$ values for the T2C*, T5C* and TobH* end-members, for the dissociation reaction eq.(24), are -11.6, -10.5 and -7.9 respectively.

6. Application of the thermodynamic model in GEM-Selektor

6.1 Approach

The success of a thermodynamic model is measured in terms of its ability to describe the available thermochemical data in the target system(s) - here, for Ca-rich alkali-activated cements such as AAS cements and hybrid alkali-activated/PC materials - and its ability to predict the chemistry of simulated systems where experimental data are either not available or are difficult to obtain. Hence, thermodynamic models for cements must be developed using existing experimental results such as solubility measurements [8, 47], solid product assemblages [35, 37, 43], and/or the chemistry of C-(N-)A-S-H gels [42]. An extensive set of experimental solubility data in the CaO-SiO_2-H_2O system is available for the development of thermodynamic models for C-S-H gels [2-15], but the use of such information to develop models for C-(N-)A-S-H gels is significantly more complicated. Solubility measurements in the CaO-Na_2O-Al_2O_3-SiO_2-H_2O system are not available in sufficient detail to enable development of thermodynamic models using this information alone, meaning that validation against other data is necessary. In this light, AAS cements provide an opportunity to validate the thermodynamic model; these materials are described mostly in terms of the more complex CaO-Na_2O-Al_2O_3-SiO_2-H_2O-MgO system, but are relatively well characterised. Hence, the thermodynamic

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model here is validated for the less complex CaO-(Na_2O,Al_2O_3)-SiO_2-H_2O systems, and also AAS cements. The ability of the thermodynamic model to predict solid phase assemblages in these systems will be discussed in a subsequent publication.

GEM-Selektor simulations for the CaO-SiO_2-H_2O and CaO-(Na_2O,Al_2O_3)-SiO_2-H_2O systems were performed at a constant temperature and pressure of 25°C and 1 bar, using 1 g of each of the gases $O_{2\,(g)}$ and $N_{2\,(g)}$. Simulations were performed by adding H_2O, NaOH, CaO, $Al(OH)_3$ and SiO_2 at a fixed liquid/solid ratio = 50 using a basis of 1000 g H_2O. The C-(N-)A-S-H thermodynamic model developed here (CNASH_ss) was used in all simulations. This model is provided as Electronic Supplementary Information, in the correct format for use in GEM-Selektor v3. The data used for the other gases, aqueous species and solid phases included in the simulations, in addition to the C-(N-)A-S-H thermodynamic model developed here, are shown in Appendix C.

6.2 Model validation in the CaO-SiO_2-H_2O system

An extensive body of solubility data for the CaO-SiO_2-H_2O system is available [2-15], which has been used to develop thermodynamic models for C-S-H gels in the past [15, 17, 18, 22, 25]. The fit of the new model to these data (Figure 2) is very good regarding description of the available data for pH, for concentrations of [Ca] < 2 mmol/L (mM) and [Si] > 0.1 mM, and for Ca and Si solubilities up to a molar Ca/Si ratio in the solid ≈ 1.3. The thermodynamic model is less consistent with the full body of available data at higher dissolved Ca concentrations, lower aqueous Si concentrations, and higher Ca/Si ratios in the solid, but matches more closely with the more recently published data, particularly the measurements reported in [8]. The poorer fit of the thermodynamic model to these data indicate that it is partly limited by the assumption of no additional solid solution $Ca(OH)_2$; the simulated C-S-H gels are in equilibrium with portlandite for Ca/Si > 1.4 and amorphous SiO_2 is simulated at Ca/Si ratios in the solid ≤ 0.67 (Figure 2). It has previously been proposed [8] that C-S-H solubility varies as a function of the nanostructure of this phase, which is much more pronounced for

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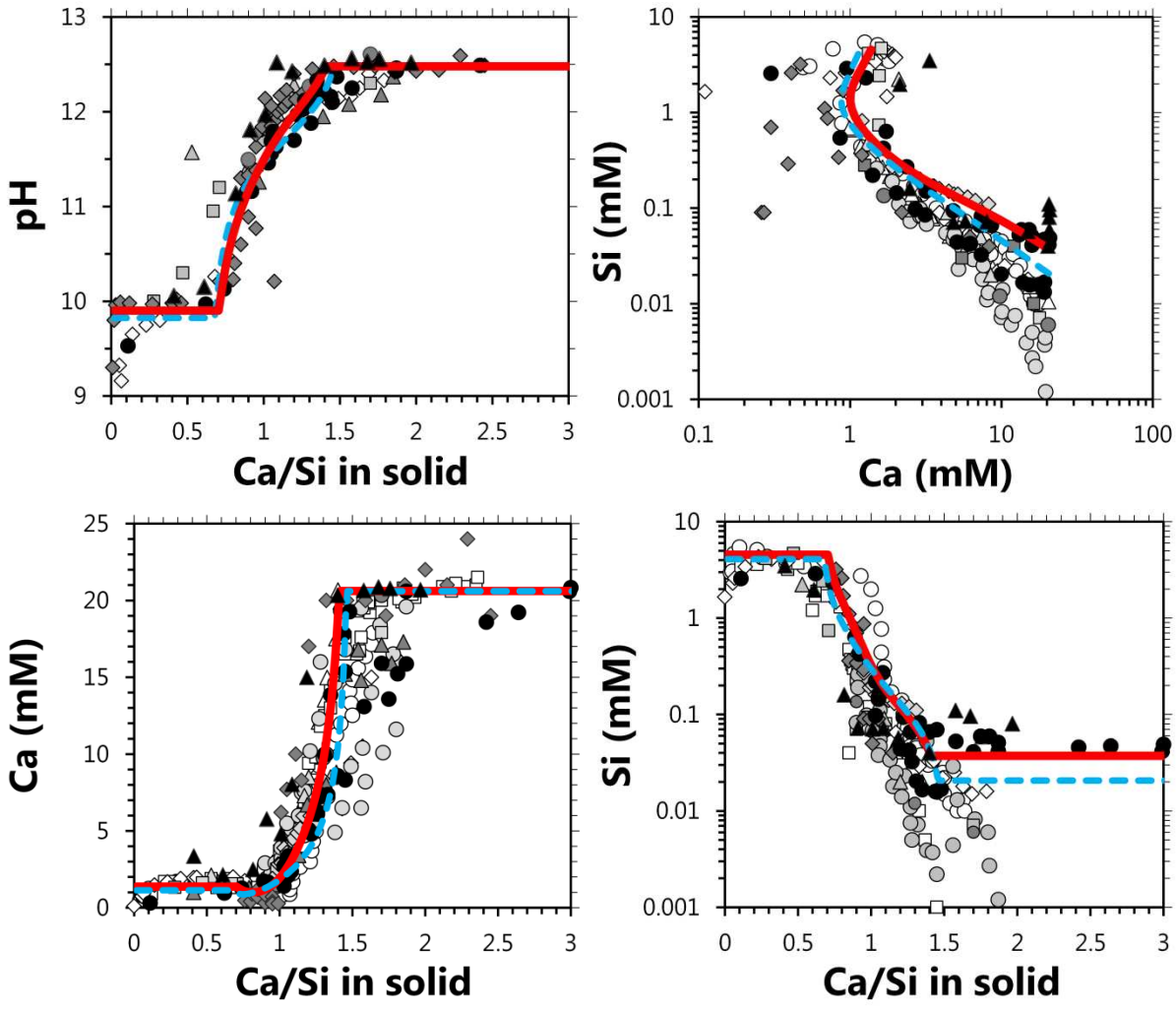
Ca/Si > 1 when many nanostructural configurations and potential bonding environments for Ca are possible (for example, Ca can be accommodated in the CB and IC sites here). This would mean that C-S-H thermodynamic models with a single curve for the solubility-structure relationships in these gels are inherently unable to describe the full range of available solubility data for this phase. However, the compositional region that is described accurately by the thermodynamic model is the region of principal importance for cementitious materials with compositions in the CaO-Na_2O-Al_2O_3-SiO_2-H_2O system, which typically contain C-(N-)A-S-H gels with Ca/Si ≤ 1.2 (as discussed in section 2).



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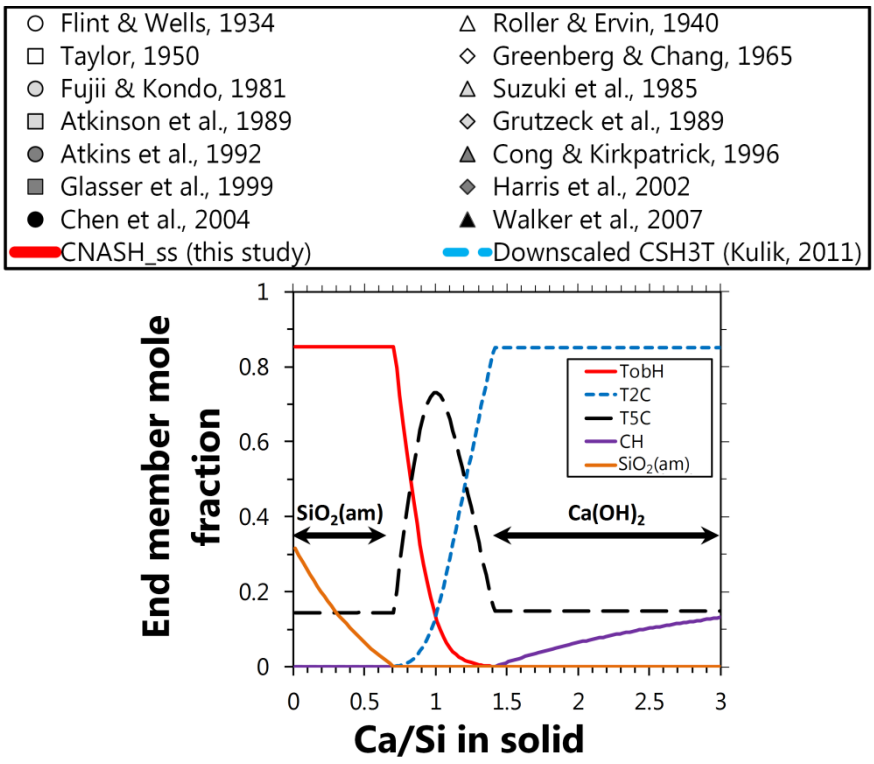

Figure 2. Comparison of the simulation results (25°C, 1 bar, water/solids mass ratio = 50) using the thermodynamic model developed here (CNASH_ss, bold red traces) to the downscaled CSH3T model (dashed blue traces) [25] and published solubility data in the CaO-SiO_2-H_2O system [2-15]. Additional plots are provided in Appendix D for the MCL and bulk chemistry results. The thermodynamic properties of the phases included in these simulations are given in Appendix C.

6.3 Model validation in the CaO-Na_2O-SiO_2-H_2O system

Significantly fewer thermochemical data are available for cements in the more complex CaO-Na_2O-SiO_2-H_2O system than in the CaO-SiO_2-H_2O system. Simulations for the CaO-Na_2O-SiO_2-H_2O system (Figure 3) were performed at bulk NaOH concentrations of 0.25, 0.5, 1 and 3 mol/L, and compared to published results in the respective ranges of [NaOH] = 0.1 – 0.3 M, 0.3 – 0.8 M, 0.8 – 1 M, 1 – 5 M. This grouping was chosen to constrain the range of NaOH concentrations in the experimental studies relatively tightly to the bulk alkali concentrations used in the simulations, while maintaining enough data points in each group to enable reliable validation of the thermodynamic model. Results for the 0.5 M NaOH simulation are shown in Figure 3, and the 0.25 M, 1 M and 3 M NaOH simulations are shown in Appendix D.

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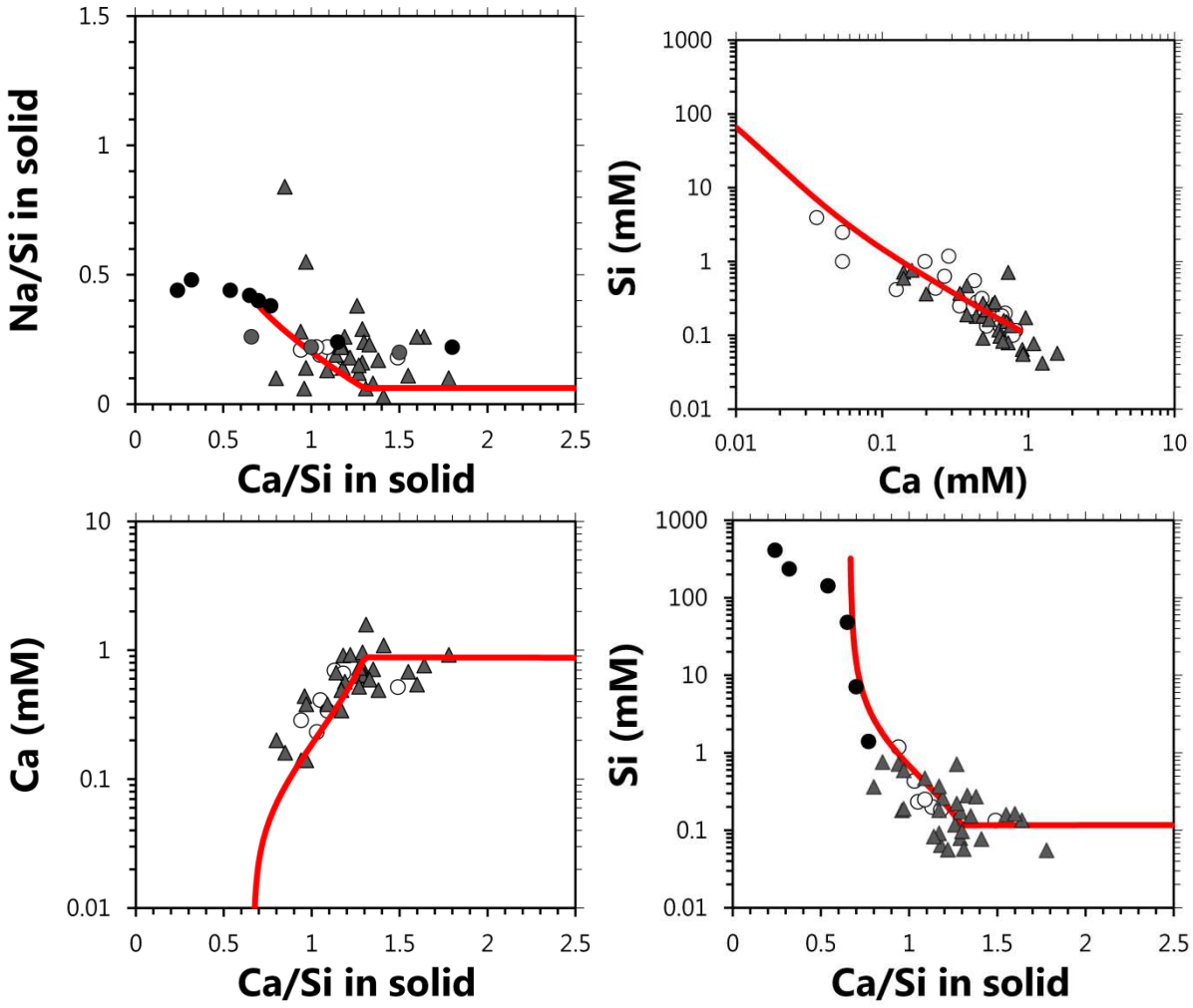
The maximum Ca content of equilibrated (sodium) calcium silicate hydrate (C-(N-)S-H) gels and the bulk system alkalinity are inversely related [75]; C-(N-)S-H gels with solid Ca concentrations above this maximum value are more soluble than portlandite at equilibrium (a maximum value of Ca/Si ≈ 1 has been reported for equilibrated C-(N-)S-H gels [75] at bulk NaOH concentrations ≈ 1 mol/kg). The thermodynamic modelling simulations performed here show this same trend (Figure 3 and Appendix D), which indicate that the C-(N-)S-H gels modelled at a bulk NaOH concentration of 3 M are in equilibrium with portlandite at all Ca/Si ratios ≥ 1, rather than the much higher Ca/Si ratios at which this is observed in the $CaO\text{-}SiO_2\text{-}H_2O$ system (Ca/Si ≥ 1.4, Figure 2).



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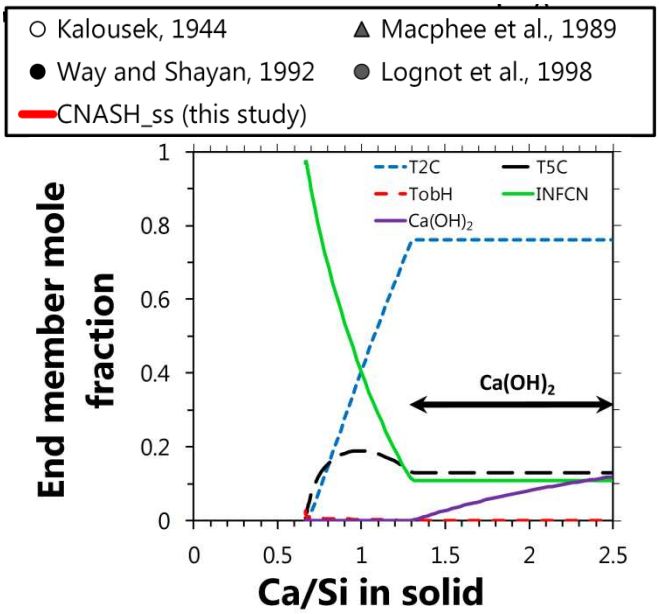

Figure 3. Comparison of the simulation results (25°C, 1 bar, 0.5 M NaOH/solids mass ratio = 50) using the thermodynamic model developed here (CNASH_ss, bold red traces) to published solubility data in the CaO-Na_2O-SiO_2-H_2O system at alkali concentrations 0.3 M ≤ [NaOH] ≤ 0.8 M [76, 77, 80, 81]. The simulated C-S-H gels are in equilibrium with portlandite at molar ratios of Ca/Si in the solid ≥ 1.3. Additional plots are provided in Appendix D for the bulk chemistry results. The thermodynamic properties of the phases included in these simulations are given in Appendix C.

The good agreement between the measured solubility data for NaOH concentrations of 0.3 M-0.8 M and the simulation at [NaOH] = 0.5 M is evident in Figure 3. The composition of the simulated C-(N-)S-H gel also captures the relatively higher Na content measured in this phase at lower Ca/Si ratios [77]. The comparisons between the simulated and reported solubility data in the other alkali concentration ranges studied are also good (Appendix D), with the exception of some of the data reported at NaOH concentrations > 1 M in [80]. This may be explained by the presence of additional sodium calcium silicate hydrate gels in those highly alkaline systems that are not described in the thermodynamic databases used here (e.g. phases with similarities to the kanemite group of minerals [85], which are thought to be similar to alkali-aggregate reaction products). This would mean that the aqueous composition data for [NaOH] concentrations > 1 M in [80] may not be solely determined by the solubility of C-(N-)S-H phases.

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6.4 Model validation in the $CaO-Al_2O_3-SiO_2-H_2O$ system

Analysis of C-A-S-H gel solubility from published solubility data for this phase [41, 86] is complicated by the coexistence of secondary phases such as strätlingite and/or superficial carbonation products (e.g. calcium hemicarboaluminate, $C_4Ac_{0.5}H_{12}$) in the solids analysed. Here, the thermodynamic model is validated against the solubility dataset published by Pardal et al. [41] (Figure 4) over the bulk composition range most relevant for AAS cements, $0.66 \leq Ca/(Al+Si) \leq 1$ and $0 \leq Al/Si \leq 0.33$. The simulation results and the measured solubility data are comparable, to within an order of magnitude. These data show a similar inverse relationship between [Si] and [Ca] to that described by the solubility data for these elements in the $CaO-SiO_2-H_2O$ system (Figure 2).

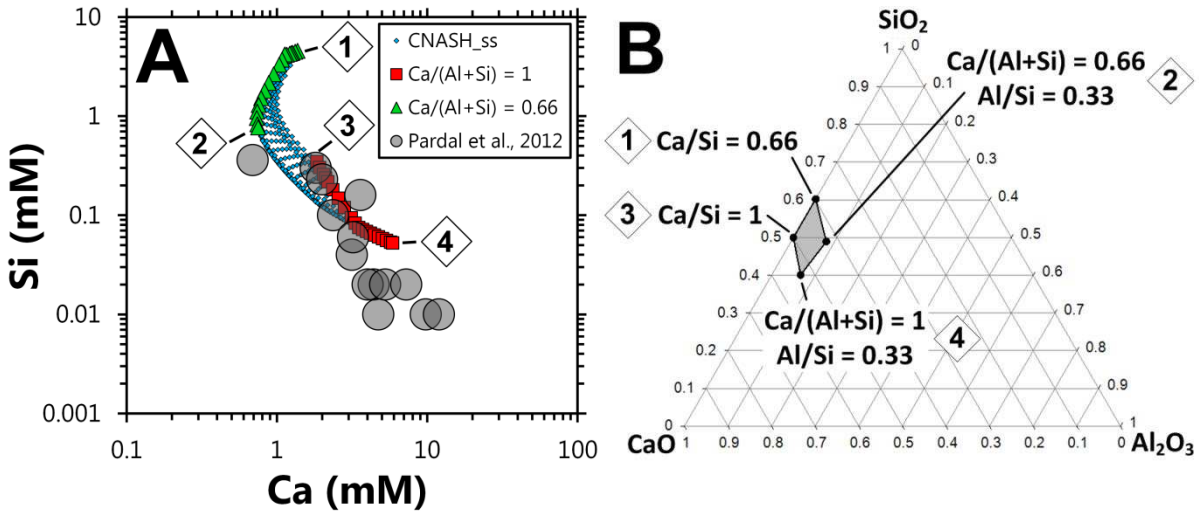

Figure 4. A) Comparison of the simulation results (25°C, 1 bar, water/solids mass ratio = 50) using the thermodynamic model developed here (CNASH_ss, small blue diamonds, red squares and green triangles) to published solubility data for C-A-S-H gels in the $CaO-Al_2O_3-SiO_2-H_2O$ system (large grey circles [41]). The corresponding range of bulk compositions simulated, projected onto the $CaO-SiO_2-Al_2O_3$ ternary system, is shown in B). The thermodynamic properties of the phases included in these simulations are given in Appendix C.

Chemical composition data for C-A-S-H gels are also used for model validation [42, 48, 78, 79]; most of these data exist at three bulk Al/Si compositions: $Al/Si \approx 0.1$, 0.2 and 0.33. Comparison of the modelling results against these data (Figures 5A-5C), for the relevant composition range in AAS

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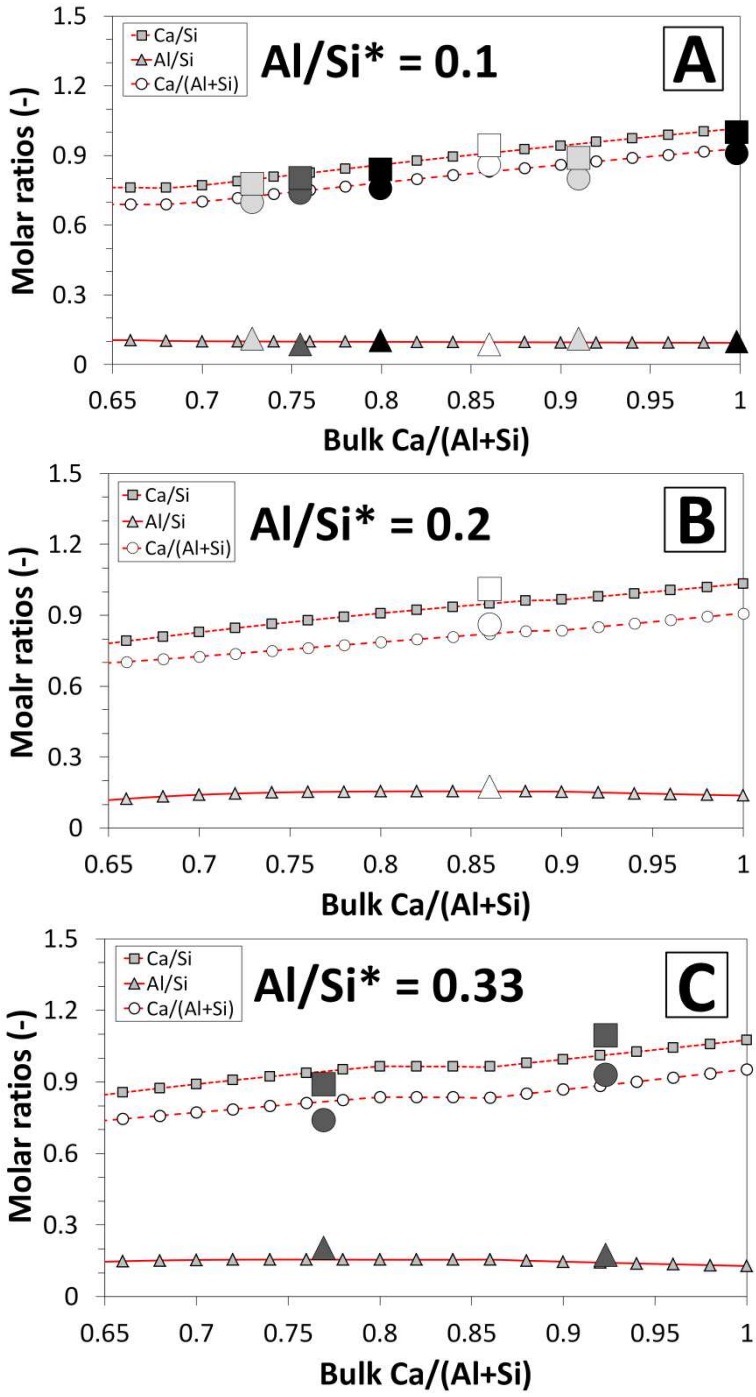
597 binders (0.65 ≤ bulk Ca/(Al+Si) ≤ 1), shows that the simulations accurately describe all of the
598 reported chemical composition data for this phase.

599



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601

602

603 **Figure 5**. Comparison of the simulation results (25°C, 1 bar, water/solids mass ratio = 50) using the
604 thermodynamic model developed here (CNASH_ss, small symbols and red lines) to the published
605 chemical composition data for C-A-S-H gels (large symbols represent data from the literature: white
606 [42]; light grey [78]; dark grey [48]; black [79]). Al/Si* = bulk Al/Si. Additional plots are provided in

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Appendix D for the end-member compositions. The thermodynamic properties of the phases included in these simulations are given in Appendix C.

6.5 Model validation in AAS cement systems

Simulations for calculating the solubility of AAS cements were performed in an N_2 atmosphere (1 g of $N_{2\ (g)}$, to avoid oxidation of the system) at 25°C, 1 bar and at water/binder ratios specified as reported in the literature (Appendix E). Congruent slag dissolution was assumed, with the slag reaction extents and bulk chemical compositions simulated by proportional additions of SiO_2, CaO, MgO, Al_2O_3, Na_2O, K_2O, and H_2SO_4 or dissociated $H_2S_{(aq)}$ (matching the SO_4^{2-} and S^{2-} content in the slag where reported, otherwise all sulfur is assumed to be present as S^{2-}), to match the bulk slag chemical compositions and reaction extents reported in the literature (e.g. [45, 87, 88]). All other components of the slag were excluded, as the concentrations of other elements in the slags studied are minor and the reactivity of Fe entrained in slag appears to be very low [89]. For the cases where the degree of reaction of the slag is needed but not available, the extent of reaction of the slag was set so that the bulk chemistry of the simulations matched the bulk chemistry of the binder gel assumed in the original work [50], or estimated where no further information was available (using the reaction extents provided in [87] as reference values, then modifying based on the bulk alkalinity and curing time).

The simulated solubility results (Figure 6) match the experimentally-measured solubility data to approximately ±1 order of magnitude, with the poorest agreement found for the aqueous Si species in $Na_2O{\cdot}mSiO_2{\cdot}xH_2O$-activated cements, which are under-predicted by the thermodynamic model. However, the uncertainty associated with each experimental data point is expected to be large, possibly also up to one order of magnitude, because slag reaction extents are not quantified in the experimental studies referenced here (with the exception of the estimations in [87] for the data in [71]) and the data correspond to systems that are quite far from equilibrium in some cases (e.g. samples were cured for 7 days in [82]). Similar slag reaction degrees to those estimated here (~40%

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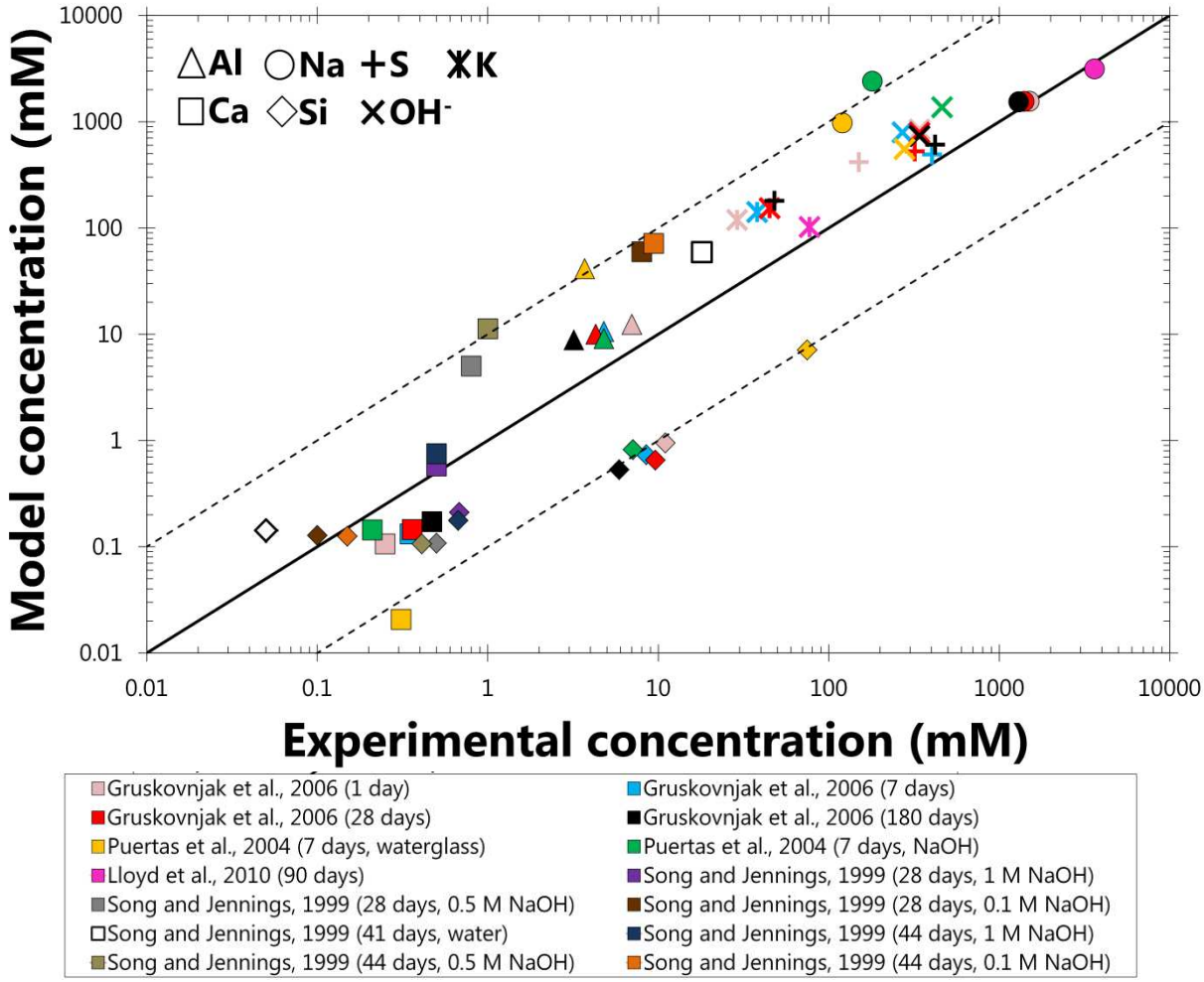
634 at 100 days of curing) have been observed in sodium silicate and NaOH-activated slag pastes (35%-
635 45% at 100 days of curing [44]), which does indicate that the estimates used here are reasonable,
636 but does not fully resolve the uncertainty attributed to this factor. With this in mind, the accuracy of
637 the fit between the simulation and experimental results is similar to the level of uncertainty that can
638 be expected for modelling dissolved elemental concentrations in AAS cements.
639



640
641

642 **Figure 6**. Simulated elemental concentrations in the aqueous phase compared to experimental pore
643 solution composition data for AAS cements [71, 82-84]. The dotted lines show ±1 order of
644 magnitude deviation from the solid y = x line. The thermodynamic properties of the phases included
645 in these simulations are given in Appendix C. The slag reaction extents used in these simulations are
646 shown in Appendix E.
647

648 Comparisons between thermodynamic modelling results and experimental measurements of C-(N-
649)A-S-H gel chemical compositions in AAS cements are not straightforward because secondary

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products are often intimately intermixed with C-(N-)A-S-H gel in these materials [27] and because the nanostructure and chemical composition of this phase can vary considerably at extended ages [39]. In this sense, thermodynamic modelling can play an important role in understanding how the solid phase assemblage and chemical composition of C-(N-)A-S-H gel may change over time, with simulation results representing the predicted nature of the solid binder at equilibrium.

It is also important to assess how accurately the thermodynamic model represents the bulk volumetric properties of C-(N-)A-S-H gels, because this is a central aspect of the application of thermodynamic modelling to cement-based materials [90]. The C-(N-)A-S-H gels formed in AAS cements are significantly denser than the C-S-H gels formed in neat PC materials [50], which is a result that should be embodied in thermodynamic models for this phase. Hence simulations using the thermodynamic model developed here are compared to the available volumetric data for C-(N-)A-S-H gels in AAS cements (Table 3).

Table 3. Simulated C-(N-)A-S-H gel properties in AAS cements [45, 50, 88] compared to the results reported in [50], using the bulk chemistry described in that study. The thermodynamic properties of the relevant phases in these simulations are given in Appendix C.

Activator	Curing time (days)	Density (g/cm^3)	Molar volume (cm^3/mol Si in C-(N-)A-S-H)	Reference
Experimental values				
$Na_2O{\cdot}1.82SiO_2{\cdot}xH_2O$	90	2.73	50.8	[50]
Simulated values				
$Na_2O{\cdot}1.82SiO_2{\cdot}xH_2O$	90	2.6	58	[50]
Na_2SiO_3	180	2.7	53	COL-GBFS, [88]
Na_2SiO_3	180	2.7	54	AUS-GBFS, [88]
Na_2SiO_3	180	2.7	53	SP-GBFS, [88]
NaOH	100	2.6	57	[45]
$Na_2SiO_3{\cdot}5H_2O$	100	2.5	56	[45]

The C-(N-)A-S-H bulk densities and molar volumes simulated by thermodynamic modelling are similar to the reported volumetric properties of this phase (Table 3) [50]. This result is consistent with a much more tightly packed atomic structure for the C-(N-)A-S-H gels formed in AAS cements

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671 than for the C-S-H gels formed in neat PC materials ($(CaO)_{1.7}(SiO_2)_1(H_2O)_{1.8}$, molar volume = 72.1
672 cm^3/mol [91]). This is also consistent with the discussion presented in [50], where it was argued that
673 the reported density and molar volume of the C-S-H type gels formed in AAS cements are only
674 weakly related to the bulk composition of these materials. Therefore, it can be expected that the
675 thermodynamic model developed here is able to closely represent the bulk volumetric properties of
676 C-(N-)A-S-H gels in AAS cements.
677

678 ## 6.6 Discussion and perspectives

679 This paper represents the first step towards developing a structurally-consistent thermodynamic
680 model for C-(N-)A-S-H gel that contains explicit descriptions of Al and alkali components, which
681 provides a relatively simple basis for further development and utilisation. Therefore, there are a
682 number of aspects that would improve the thermodynamic model, and some are listed here to guide
683 future development:

684 • The thermodynamic model has been designed for C-(N-)A-S-H gels with significant Al and
685 alkali incorporation, particularly those formed in AAS cement. This model may also be
686 relevant to high volume blended PC/SCM materials reacted with either water or an alkali
687 source (e.g. CEM III blast furnace cements as specified in EN 197-1), as the bulk chemical
688 compositions of these materials and AAS cements can be similar (Ca/(Al+Si) ≈ 1) [92]. Its
689 suitability for use in simulating the chemistry of these materials needs to be assessed
690 further.

691 • Improvement can be found by removing the assumptions used to simplify the mixing
692 relationships for the sublattice solid solution model, which approximated the Gibbs free
693 energies of the reciprocal reactions and the excess Gibbs free energies to zero. This will
694 become possible as more information is obtained about the energetic differences arising
695 between hypothetical end-members (i.e. energetic information regarding Si-for-Al

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696 substitution in chain sites, and (Ca^{2+},$2Na^{+}$,$2H^{+}$) substitution in interlayer sites) and the
697 solubility of C-(N-)A-S-H gels.

698 • The utility of the pore solution composition data used to parameterise the thermodynamic
699 model in AAS cements would be significantly improved if such data were published
700 alongside quantification of the reaction extent of the slag. This information, along with more
701 solubility data for AAS cements and synthetic CaO-Na_2O-Al_2O_3-SiO_2-H_2O systems, will be
702 needed to enable further development of thermodynamic models for C-(N-)A-S-H gels.

703

704

705 # 7. Conclusions

706

707 This paper has presented a thermodynamic model for the C-(N-)A-S-H gel in AAS cements, which for
708 the first time accounts explicitly for the structurally-incorporated Al and Na species in this phase.
709 This model represents C-(N-)A-S-H gel as an ideal solid solution of tobermorite-like end-members
710 with independent substitution of tetrahedral Al and Na species allowed in its formulation, meaning
711 that it may also be applicable to cement-based materials that are less alkali- and/or Al-rich than AAS
712 cements. The model was implemented in GEM-Selektor using thermodynamic properties for the C-
713 (N-)A-S-H end-members that were parameterised to match a comprehensive set of solubility data in
714 the CaO-(Na_2O,Al_2O_3)-SiO_2-H_2O and AAS cement systems, and published chemical compositions of C-
715 A-S-H gels.

716

717 A good fit was found between the full set of data used in the parameterisation procedure and the
718 simulation results, which were within ±1 order of magnitude in simulations of aqueous phase
719 chemical compositions in AAS cements, indicating that the model is suitable for thermodynamic
720 modelling of these materials. The molar volume and density of the C-(N-)A-S-H gels simulated by the
721 model were also in close agreement with the available data for this phase in AAS cements, meaning

that the model can describe chemical shrinkage in these systems. Therefore, the thermodynamic model developed here greatly improves the scope of thermodynamic modelling applications to Ca-rich alkali-activated cements and hybrid alkali-activated/PC materials, which is important for understanding the durability of these materials under sealed, ambient and aggressive environmental conditions.

8. Supporting information

The GEM-Selektor database files for the thermodynamic model developed here (CNASH_ss) are provided as Electronic Supplementary Information, which can be accessed via the journal website (http://www.journals.elsevier.com/cement-and-concrete-research/).

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Appendix A. Additional details of the C-(N-)A-S-H sublattice solid solution model

Derivation of the C-(N-)A-S-H thermodynamic model begins by rearranging the SGM (eq.(A1), [38]) into an alternative structural form:

$$Ca_X H_{(6n-2X)} \left(Si_{(1-a_0)} R_{a_0}\right)_{(3n-1)} O_{(9n-2)} \cdot l^{c+}_{\frac{a_0}{c}(3n-1)} \cdot zCa(OH)_2 \cdot mH_2O \quad \text{(A26)}$$

where R is a trivalent cation in tetrahedral coordination (e.g. Al^{3+}), l is a charge-balancing interlayer cation (such as Ca^{2+}) with a positive charge of c, m defines the amount of bound interlayer water, n is the number of dreierketten units per non-crosslinked C-(N-)A-S-H chain, a_0 is the extent of substitution in aluminosilicate chains and the parameters X, z, a_0 and n are defined according to eq.(A2):

$$\left.\begin{aligned} X &= 0.5(6n-w) \\ z &= 0.5\left[w+n(y-2)\right] \\ 0 \le a_0 &\le \frac{n-1}{(3n-1)} \end{aligned}\right\} \quad \text{(A27)}$$

The parameters w and y are related to the extent of protonation of chain tetrahedra and amount of solid solution $Ca(OH)_2$ present in the gel. Rearrangement of the SGM begins by normalising eq.(A1) to a basis of one dreierketten unit by dividing by n, expressed in terms of w and n for X and z, and then simplified to obtain eq.(A3):

$$Ca_{\left(3-\frac{w}{2n}\right)} H_{\left(\frac{w}{n}\right)} O_{\left(9-\frac{2}{n}\right)} \cdot \left(Si_{(1-a_0)} R_{a_0}\right)_{\left(3-\left(\frac{1}{n}\right)\right)} l^{c+}_{\frac{a_0}{c}\left(3-\frac{1}{n}\right)} \cdot \left(\frac{w}{2n} - \frac{y}{2} - 1\right) Ca(OH)_2 \cdot \left(\frac{m}{n}\right) H_2O \quad \text{(A28)}$$

The following notation is now introduced into eq.(A3): $v = 1/n$ ($0 \le v \le 1$), defines the ratio of chains per dreierketten unit, which is a measure of the number of vacant bridging tetrahedra; $u = w/n$, the

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content of chemically incorporated (hydroxyl) water per dreierketten unit; and $h = m/n$, the bound water content. The introduction of this notation results in eq.(A4):

$$Ca_{\left(3-\frac{u}{2}\right)}H_uO_{(9-2\nu)}\cdot\left(Si_{(1-a_0)}R_{a_0}\right)_{(3-\nu)}\cdot l^{c+}_{\frac{a_0}{c}(3-\nu)}\left(\frac{u}{2}-\frac{y}{2}-1\right)Ca(OH)_2\ hH_2O \qquad \text{(A29)}$$

Eq.(A4) is then re-written to isolate two distinct sublattice sites within the chain structure, being a 'main chain dreierketten unit' (TU) and a 'bridging tetrahedral unit' (BT). This leads to a subtle change in the substitution parameter, a_0, which is now written as a, the extent of substitution in bridging sites. The resulting equation is:

$$\left[Ca(OH)_2\right]_{\left(\frac{u+y-2}{2}\right)}\cdot\left[\left(CaSiO_{3.5}\right)_2^-\right]\cdot\left[\left(Si_{(1-a)}R_aO_2\right)_{(1-\nu)}\right]^{a(1-\nu)-}\cdot\left[\left(l^{c+}_{\frac{a}{c}(1-\nu)}\right)\right]^{a(1-\nu)+}\cdot\left[Ca_{\left(1-\frac{u}{2}\right)}H_u\right]^{2+}\cdot hH_2O \qquad \text{(A30)}$$

Eq.(A5) is equivalent to eq.(2) in the main body of the text.

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Appendix B. Activity coefficient relationships for the C-(N-)A-S-H end-members

The relationships for the fictive activity coefficients for the end-members of the C-(N-)A-S-H sublattice solid solution model are defined here in terms of the following notation: 5CA = 0, INFCA = 1, 5CNA = 2, INFCNA = 3, INFCN = 4, T2C* = 5, T5C* = 6, TobH* = 7.

$$\ln(\lambda_0) = 2\ln(\chi_0+\chi_1)+2\ln(\chi_0+\chi_1)+2\ln(\chi_0+\chi_2+\chi_5+\chi_6)+ \ln(\chi_0+\chi_5+\chi_6)+\ln(\chi_0+\chi_5+\chi_6)+\ln(\chi_0+\chi_1+\chi_2+\chi_3+\chi_4)-\ln(\chi_0) \quad \text{(B31)}$$

$$\ln(\lambda_1) = 2\ln(\chi_0+\chi_1)+2\ln(\chi_0+\chi_1)+2\ln(\chi_1+\chi_4+\chi_7)+ \ln(\chi_1)+\ln(\chi_1+\chi_4+\chi_7)+\ln(\chi_0+\chi_1+\chi_2+\chi_3+\chi_4)-\ln(\chi_1) \quad \text{(B32)}$$

$$\ln(\lambda_2) = 2\ln(\chi_2+\chi_3)+2\ln(\chi_2+\chi_3)+2\ln(\chi_0+\chi_2+\chi_5+\chi_6)+ \ln(\chi_2)+\ln(\chi_2)+\ln(\chi_0+\chi_1+\chi_2+\chi_3+\chi_4)-\ln(\chi_2) \quad \text{(B33)}$$

$$\ln(\lambda_3) = 2\ln(\chi_2+\chi_3)+2\ln(\chi_2+\chi_3)+2\ln(\chi_3)+ \ln(\chi_3)+\ln(\chi_3)+\ln(\chi_0+\chi_1+\chi_2+\chi_3+\chi_4)-\ln(\chi_3) \quad \text{(B34)}$$

$$\ln(\lambda_4) = 2\ln(\chi_4)+2\ln(\chi_4)+2\ln(\chi_1+\chi_4+\chi_7)+ \ln(\chi_4)+\ln(\chi_1+\chi_4+\chi_7)+\ln(\chi_0+\chi_1+\chi_2+\chi_3+\chi_4)-\ln(\chi_4) \quad \text{(B35)}$$

$$\ln(\lambda_5) = 2\ln(\chi_5)+2\ln(\chi_5)+2\ln(\chi_0+\chi_2+\chi_5+\chi_6)+ \ln(\chi_0+\chi_5+\chi_6)+\ln(\chi_0+\chi_5+\chi_6)+\ln(\chi_5+\chi_6+\chi_7)-\ln(\chi_5) \quad \text{(B36)}$$

$$\ln(\lambda_6) = 2\ln(\chi_6+\chi_7)+2\ln(\chi_6+\chi_7)+2\ln(\chi_0+\chi_2+\chi_5+\chi_6)+ \ln(\chi_0+\chi_5+\chi_6)+\ln(\chi_0+\chi_5+\chi_6)+\ln(\chi_5+\chi_6+\chi_7)-\ln(\chi_6) \quad \text{(B37)}$$

$$\ln(\lambda_7) = 2\ln(\chi_6+\chi_7)+2\ln(\chi_6+\chi_7)+2\ln(\chi_1+\chi_4+\chi_7)+ \ln(\chi_7)+\ln(\chi_1+\chi_4+\chi_7)+\ln(\chi_5+\chi_6+\chi_7)-\ln(\chi_7) \quad \text{(B38)}$$

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Appendix C. Thermodynamic properties of the constituent phases and the relevant phases for thermodynamic modelling in this work

The solid constituents used in the additivity method and eq.(23), to estimate the standard absolute isobaric heat capacity and absolute entropy at standard state of the C-(N-)A-S-H end-members, are shown in Table C1. The gases, aqueous species and solid phases used in the thermodynamic modelling simulations are shown in Tables C2-C4.

Table C1. Thermodynamic properties of the solid constituents used to estimate Cp^o and S^o for the C-(N-)A-S-H end-members. The reference state is 298.15 K and 1 bar.

Phase	$V°$ (cm^3/mol)	$\Delta_f H°$ (kJ/mol)	$\Delta_f G°$ (kJ/mol)	$S°$ (J/mol.K)	$Cp°$ (J/mol.K)	Reference
Portlandite, $Ca(OH)_2$	33.1	-984.7	-897.0	83.4	87.5	[93]
Amorphous SiO_2	29.0	-903.3	-848.9	41.3	44.5	[17, 94]
Gibbsite, $Al(OH)_3$	32.0	-1289	-1151	70.1	93.1	[94]
$NaOH_{(s)}$	18.8	-425.8	-379.6	64.4	59.5	[93, 95]
T2C, $(CaO)_{1.5}(SiO_2)_1(H_2O)_{2.5}$	80.6	-2722	-2467	167	237	[25]

Table C2. Thermodynamic properties of the gases used in the thermodynamic modelling simulations. The reference state is 298.15 K and 1 bar.

Gas	$V°$ (cm^3/mol)	$\Delta_f H°$ (kJ/mol)	$\Delta_f G°$ (kJ/mol.K)	$S°$ (J/mol.K)	$Cp°$ (J/mol.K)	Reference
N_2	24790	0	0	191.6	29.1	[96]
O_2	24790	0	0	205.1	29.3	[96]
H_2	24790	0	0	130.7	28.8	[96]

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Table C3. Thermodynamic properties of the aqueous species used in the thermodynamic modelling simulations. The reference state is unit activity in a hypothetical one molal solution referenced to infinite dilution at any temperature and pressure for aqueous species [70].

Species	$V°$ (cm³/mol)	$\Delta_f H°$ (kJ/mol)	$\Delta_f G°$ (kJ/mol.K)	$S°$ (J/mol.K)	$Cp°$ (J/mol.K)	Reference
Al^{3+}	-45.2	-530.6	-483.7	-325.1	-128.7	[97]
AlO^+ (+ H_2O = $Al(OH)_2^+$)	0.3	-713.6	-660.4	-113	-125.1	[97]
AlO_2^- (+ $2H_2O$ = $Al(OH)_4^-$)	9.5	-925.6	-827.5	-30.2	-49	[97]
$AlOOH^o$ (+ $2H_2O$ = $Al(OH)_3^o$)	13	-947.1	-864.3	20.9	-209.2	[97]
$AlOH^{2+}$	-2.7	-767.3	-692.6	-184.9	56	[97]
$AlHSiO_3^{2+}$ (+ H_2O = $AlSiO(OH)_3^{2+}$)	-40.7	-1718	-1541	-304.2	-215.9	[64]
$AlSiO_4^-$ (+ $3H_2O$ = $AlSiO(OH)_6^-$)	25.5	-1834	-1681	11.1	-4.6	[64]
$AlSO_4^+$	-6.0	-1423	-1250	-172.4	-204.0	[64]
$Al(SO_4)_2^-$	31.1	-2338	-2006	-135.5	-268.4	[64]
Ca^{2+}	-18.4	-543.1	-552.8	-56.5	-30.9	[97]
$CaOH^+$	5.8	-751.6	-717	28	6	[97]
$Ca(HSiO_3)^+$ (+ H_2O = $CaSiO(OH)_3^+$)	-6.7	-1687	-1574	-8.3	137.8	[98]
$CaSiO_3^o$ (+ H_2O = $CaSiO_2(OH)_2^o$)	15.7	-1668	-1518	-136.7	88.9	[64]
$CaSO_4^o$	4.7	-1448	-1310	20.9	-104.6	[98]
K^+	9.0	-252.1	-282.5	101	8.4	[97]
KOH^o	15	-474.1	-437.1	108.4	-85	[97]
KSO_4^-	27.5	-1159	-1032	146.4	-45.1	[98]
Na^+	-1.2	-240.3	-261.9	58.4	38.1	[97]
$NaOH^o$	3.5	-470.1	-418.1	44.8	-13.4	[97]
$NaSO_4^-$	18.6	-1147	-1010	101.8	-30.1	[64]
$HSiO_3^-$ (+ H_2O = $SiO(OH)_3^-$)	4.5	-1145	-1014	20.9	-87.2	[98]
SiO_2^o	16.1	-887.9	-833.4	41.3	44.5	[17, 99]
SiO_3^{2-} (+ H_2O = $SiO_2(OH)_2^{2-}$)	34.1	-1099	-938.5	-80.2	119.8	[64]
$S_2O_3^{2-}$	27.6	-649.9	-520.0	66.9	-238.5	[97]
HSO_3^-	33.0	-627.7	-529.1	139.7	-5.4	[97]
SO_3^{2-}	-4.1	-636.9	-487.9	-29.3	-281.0	[97]
HSO_4^-	34.8	-889.2	-755.8	125.5	22.7	[97]
SO_4^{2-}	12.9	-909.7	-744.5	18.8	-266.1	[97]
H_2S^o	35.0	-39.0	-27.9	125.5	179.2	[99]
HS^-	20.2	-16.2	12.0	68.2	-93.9	[97]
S^{2-}	20.2	92.2	120.4	68.2	-93.9	[63]
Mg^{2+}	-22.0	-465.9	-454.0	-138.1	-21.7	[97]
$MgOH^+$	1.6	-690.0	-625.9	-79.9	129.2	[97]
$MgHSiO_3^+$ (+ H_2O = $MgSiO(OH)_3^+$)	-10.9	-1614	-1477	-99.5	158.6	[97]
$MgSO_4^o$	1.8	-1369	-1212	-50.9	-90.3	[63, 97]
$MgSiO_3^o$ (+ H_2O = $MgSiO_2(OH)_2^o$)	12.1	-1597	-1425	-218.3	98.2	[63]
OH^-	-4.7	-230	-157.3	-10.7	-136.3	[97]
H^+	0	0	0	0	0	[97]
H_2O^o	18.1	-285.9	-237.2	69.9	75.4	[100]
N_2^o	33.4	-10.4	18.2	95.8	234.2	[99]
O_2^o	30.5	-12.2	16.4	109	234.1	[99]

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Table C4. Thermodynamic properties of the solid phases used in the thermodynamic modelling simulations. The reference state is 298.15 K and 1 bar.

Phase	$V°$ (cm^3/mol)	$\Delta_f H°$ (kJ/mol)	$\Delta_f G°$ (kJ/mol.K)	$S°$ (J/mol.K)	$Cp°$ (J/mol.K)	Reference
$Al(OH)_3$ (microcrystalline)	32.0	-1265	-1148	140	93.1	[101]
Portlandite, $Ca(OH)_2$	33.1	-984.7	-897	83.4	87.5	[93]
Amorphous SiO_2	29.0	-903.3	-849	41.3	44.5	[17, 94]
C_2AH_8	90.1	-5278	-4696	450	521	[101]
C_3AH_6	150	-5537	-5008	422	446	[101]
C_4AH_{13}	27.4	-8302	-7327	700	930	[66]
C_4AH_{19}	382	-1002	-8750	1120	1382	[101]
C_4AH_{10}	194	-5388	-4623	610	668	[101]
Monosulfate, C_4AsH_{12}	309	-8750	-7779	821	942	[64]
Stratlingite, C_2ASH_8	21.6	-6360	-5705	546	603	[64]
Ettringite, $C_6As_3H_{32}$	707	-17535	-15206	1900	2174	[66]
Hydrotalcite, M_4AH_{10}	220	-7196	-6395	549	649	[66]
Brucite, $Mg(OH)_2$	24.6	-923	-832	63.1	77.3	[94]
The 'downscaled CSH3T' model [a]						
TobH, $(CaO)_1(SiO_2)_{1.5}(H_2O)_{2.5}$	85.0	-2833	-2562	153	231	[25]
T5C, $(CaO)_{1.25}(SiO_2)_{1.25}(H_2O)_{2.5}$	79.3	-2782	-2519	160	234	[25]
T2C, $(CaO)_{1.5}(SiO_2)_1(H_2O)_{2.5}$	80.6	-2722	-2467	167	237	[25]

[a] The mixing rules used to describe the downscaled CSH3T model and the thermodynamic properties that define the TobH, T5C and T2C end-members in GEM-Selektor are the same as those described in [25] for this model. The Gibbs free energies (and thus the enthalpies) of these components are modified slightly to the corresponding values used to define the TobH*, T5C* and T2C* end-members of the CNASH_ss model (Table 2).

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Appendix D. Additional simulation results used to validate the thermodynamic model

Additional simulation results that were used to validate the thermodynamic model are shown in Figures D1-D6.

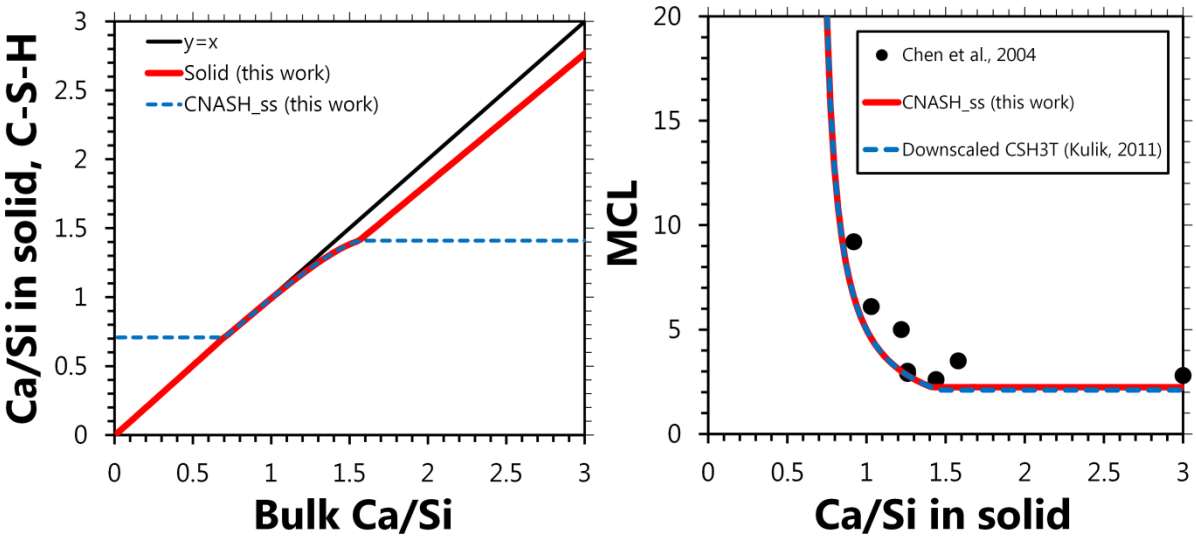

Figure D1. Simulation results (25°C, 1 bar, 0.25 M NaOH/solids mass ratio = 50) using the thermodynamic model developed here (CNASH_ss) in addition to those presented in Figure 2. The MCL calculations are compared to the data reported in [8] and the simulation results using the downscaled CSH3T model [25]. The thermodynamic properties of the phases included in these simulations are given in Appendix C.

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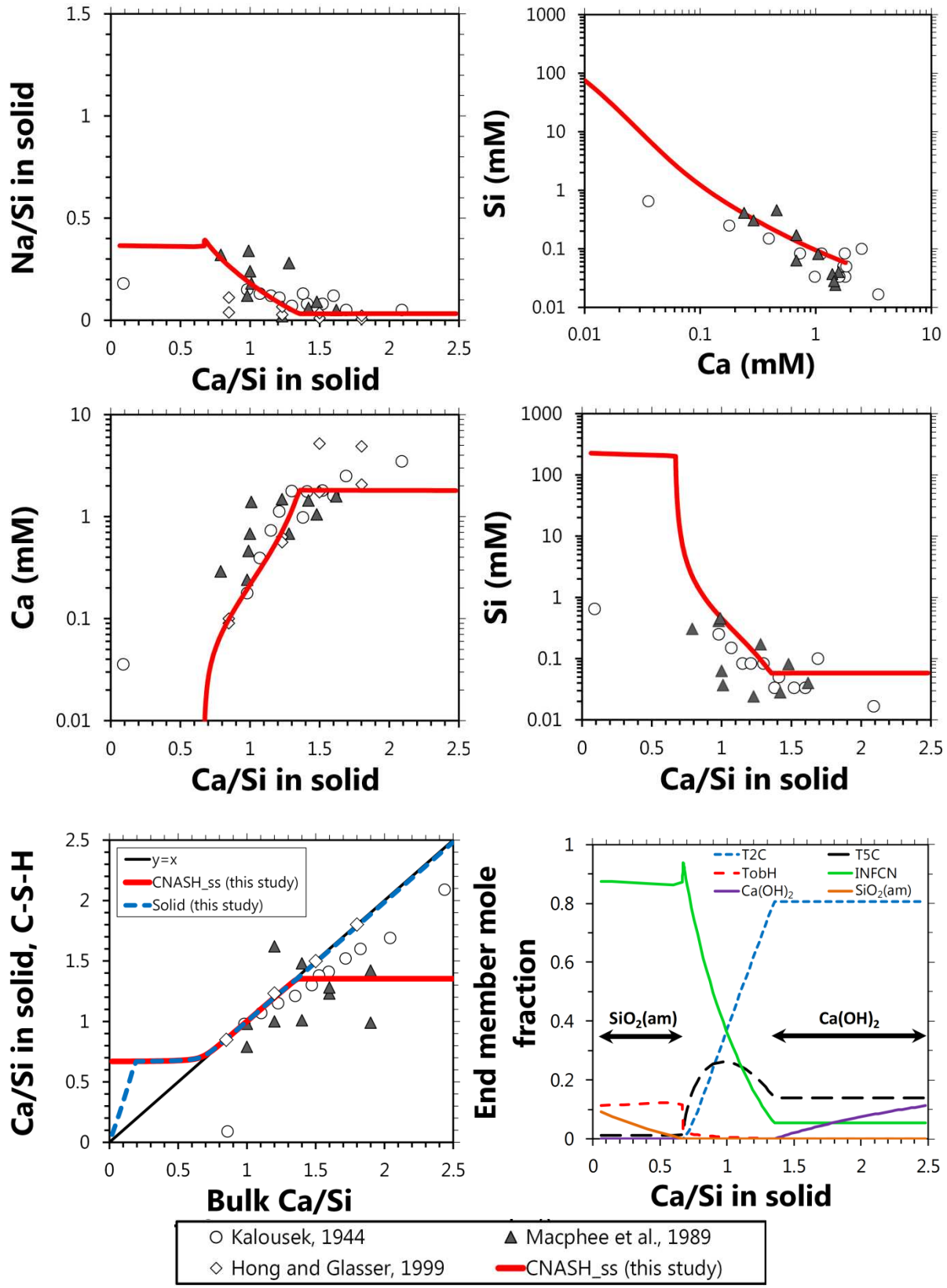

Figure D2. Comparison of the simulation results (25°C, 1 bar, 0.25 M NaOH/solids mass ratio = 50) using the thermodynamic model developed here (CNASH_ss, bold red traces) to published solubility data in the CaO-Na_2O-SiO_2-H_2O system at alkali concentrations 0.1 M ≤ [NaOH] ≤ 0.3 M [76, 80, 81]. The thermodynamic properties of the phases included in these simulations are given in Appendix C.

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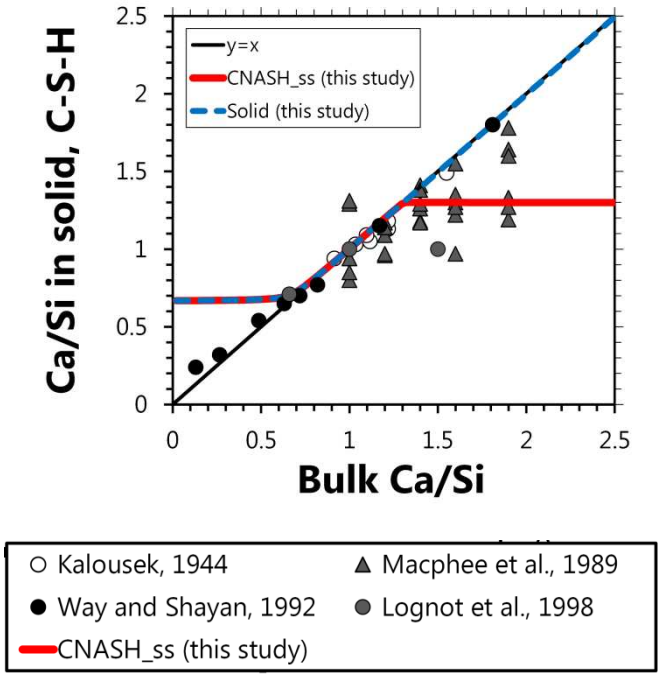

Figure D3. Comparison of the simulation results (25°C, 1 bar, 0.5 M NaOH/solids mass ratio = 50) using the thermodynamic model developed here (CNASH_ss, bold red traces) to solid chemistry data in the CaO-Na_2O-SiO_2-H_2O system at alkali concentrations 0.3 M ≤ [NaOH] ≤ 0.8 M [76, 80, 81], in addition to the results shown in Figure 3 for this system. The thermodynamic properties of the phases included in these simulations are given in Appendix C.

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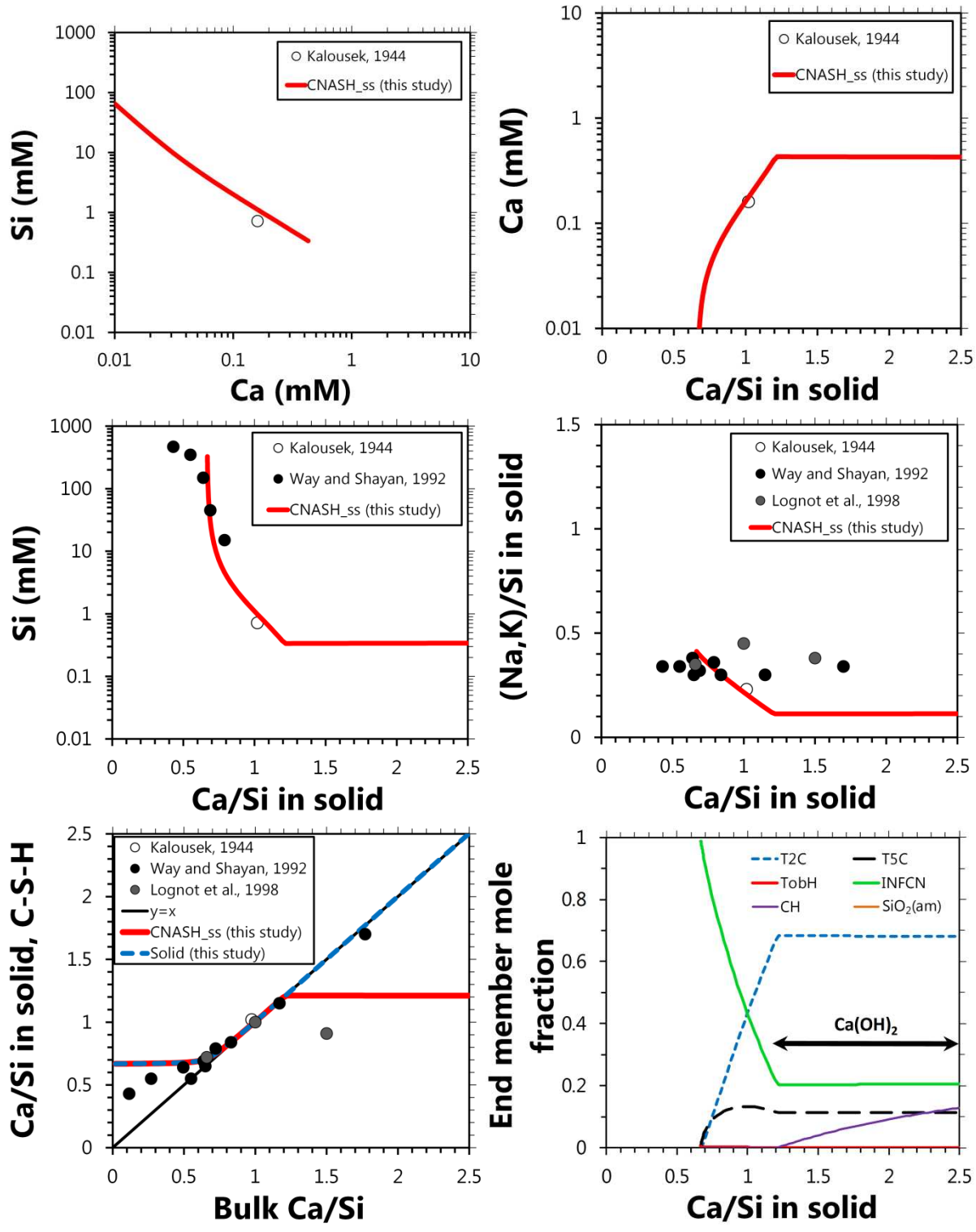

Figure D4. Comparison of the simulation results (25°C, 1 bar, 1 M NaOH/solids mass ratio = 50) using the thermodynamic model developed here (CNASH_ss, bold red traces) to solubility and solid phase chemistry data in the CaO-Na_2O-SiO_2-H_2O system at alkali concentrations 0.8 M ≤ [NaOH] ≤ 1 M [75, 77, 80]. The corresponding end member mole fraction results are also shown. The thermodynamic properties of the phases included in these simulations are given in Appendix C.

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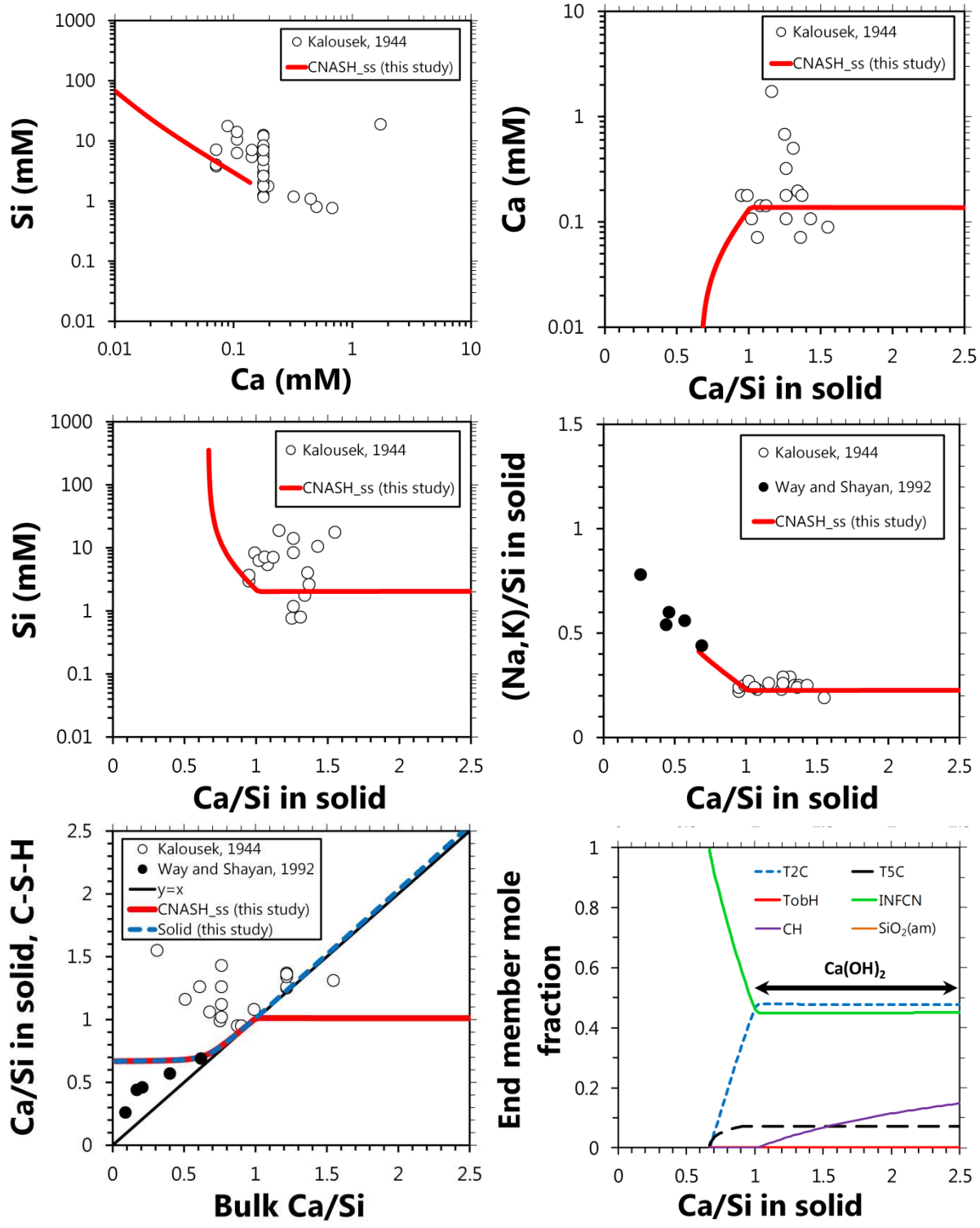

Figure D5. Comparison of the simulation results (25°C, 1 bar, 3 M NaOH/solids mass ratio = 50) using the thermodynamic model developed here (CNASH_ss, bold red traces) to solubility and solid phase chemistry data in the CaO-Na_2O-SiO_2-H_2O system at alkali concentrations 1 M ≤ [NaOH] ≤ 5 M [77, 80]. The corresponding end member mole fraction results are also shown. The thermodynamic properties of the phases included in these simulations are given in Appendix C.

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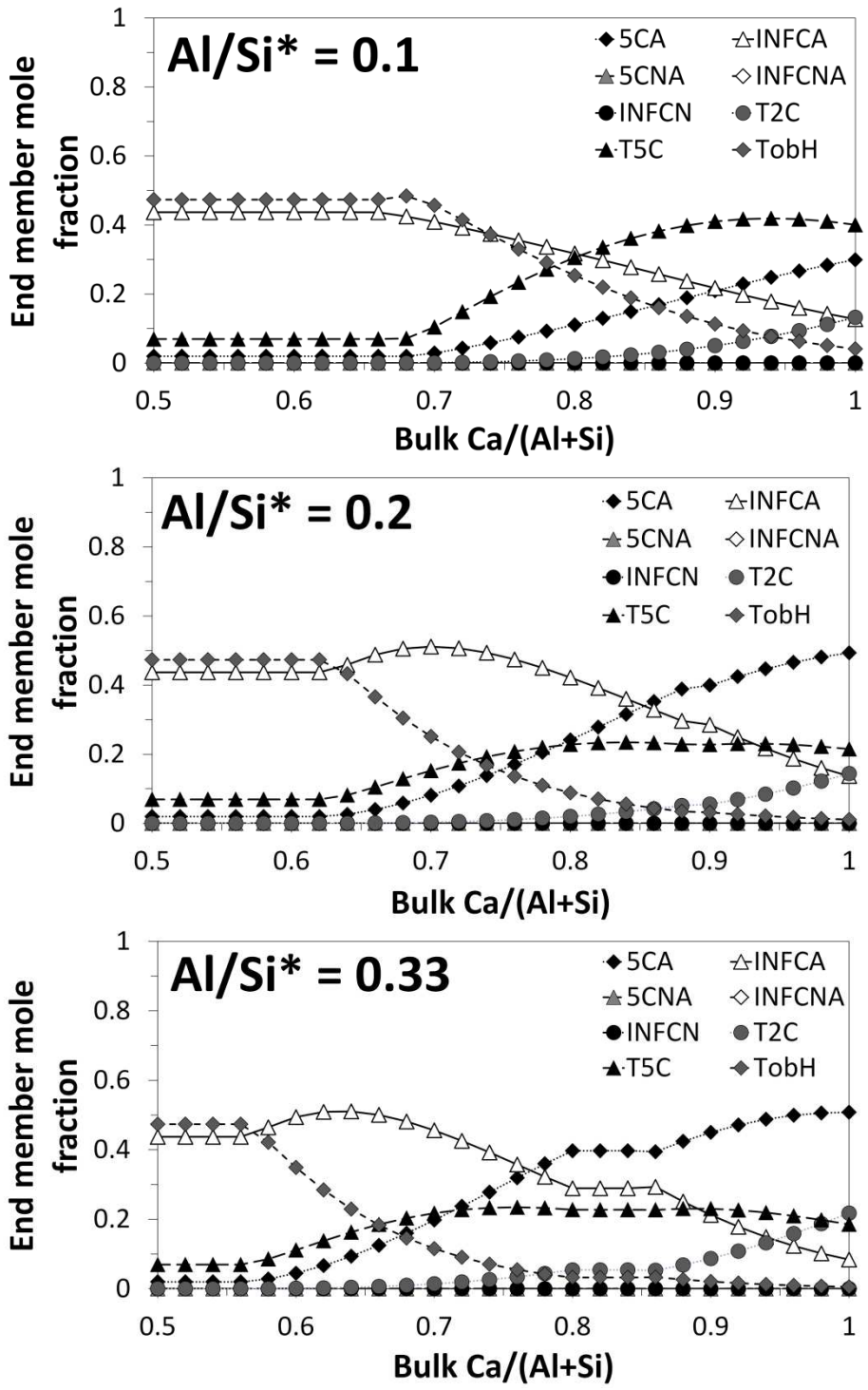

Figure D6. End member mole fractions corresponding to the simulation results shown in Figure 5 (25°C, 1 bar, water/solids mass ratio = 50). Al/Si* = bulk Al/Si. The thermodynamic properties of the phases included in these simulations are given in Appendix C.

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Appendix E. Additional details of the AAS cements simulated by thermodynamic modelling

The slag reaction extents, curing times and activating conditions used to simulate the pore solution chemistry of AAS cements (Figure 6) are shown in Table E1.

Table E1. Slag reaction extents, curing times and activating conditions used to simulate the pore solution chemistry of AAS cements.

System (corresponding to the legend labels in Figure 6)	Curing time (days)	Activator	Water/binder	Slag reaction extent used in simulations (%)	Reference
Gruskovnjak et al., 2006	1	$Na_2SiO_3.5H_2O$	0.3 [a]	32	[71]
Gruskovnjak et al., 2006	7	$Na_2SiO_3.5H_2O$	0.3 [a]	36	[71, 87]
Gruskovnjak et al., 2006	28	$Na_2SiO_3.5H_2O$	0.3 [a]	38	[71, 87]
Gruskovnjak et al., 2006	180	$Na_2SiO_3.5H_2O$	0.3 [a]	42	[71, 87]
Puertas et al., 2004	7	$Na_2O{\cdot}1.5SiO_2{\cdot}xH_2O$	0.5 [b]	36	[82]
Puertas et al., 2004	7	NaOH	0.5 [b]	36	[82]
Lloyd et al., 2010	90	$Na_2O{\cdot}mSiO_2{\cdot}xH_2O$	0.35	40	[83]
Song and Jennings, 1999	28	1 M NaOH	0.45 [c]	36	[84]
Song and Jennings, 1999	28	0.5 M NaOH	0.45 [c]	31	[84]
Song and Jennings, 1999	28	0.1 M NaOH	0.45 [c]	26	[84]
Song and Jennings, 1999	41	H_2O	0.45 [c]	21	[84]
Song and Jennings, 1999	44	1 M NaOH	0.45 [c]	39	[84]
Song and Jennings, 1999	44	0.5 M NaOH	0.45 [c]	34	[84]
Song and Jennings, 1999	44	0.1 M NaOH	0.45 [c]	29	[84]

[a] water/cement.
[b] (water + activator)/slag.
[c] liquid/slag.