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An Ideal Solid Solution Model for C-S-H

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Abstract

A model for an ideal solid solution, developed by Nourtier-Mazauric et al. [Oil & Gas Sci. Tech. Rev. IFP, 60 [2] (2005) 401], is applied to calcium-silicate-hydrate (C-S-H). Fitting the model to solubility data reported in the literature for C-S-H yields reasonable values for the compositions of the end-members of the solid solution and for their equilibrium constants. This model will be useful in models of hydration kinetics of tricalcium silicate because it is easier to implement than other solid solution models, it clearly identifies the driving force for growth of the most favorable C-S-H composition, and it still allows the model to accurately capture variations in C-S-H composition as the aqueous solution changes significantly at early hydration times.

Keywords

solubility; cement; equilibrium constant; solid solution

1. Introduction

The purpose of this paper is to present a thermodynamic model that can be used to predict the thermodynamic driving force for growth of calcium silicate hydrate (C-S-H)[†] during hydration of tricalcium silicate. Extensive study of the solubility of C-S-H, which has been reviewed by several authors^{1,2,3,4,5}, has yielded abundant data that have been interpreted in terms of solid solution models including 2 or 3 types of C-S-H with calcium/silicon atomic ratios ranging from about 0.8 (similar to tobermorite) to 2. Indeed, Richardson⁶ recently showed that the structure of C-S-H with C/S ratios < 1.5 can be understood as a stacking of sheets with infinite siloxane chains interspersed with sheets having only siloxane dimers. These would be true solid solutions of components with C/S = 2/3 and 3/2. During hydration of cement, the composition of the aqueous solution will change considerably, and the composition of the solid precipitate will change accordingly, reaching C/S ≈ 1.7. Lothenbach and Nonat⁷ argue that the observed range of C/S ratios can be achieved by removing bridging silicate tetrahedra from a tobermorite-like structure and replacing them with interlayer calcium ions, while preserving structural continuity. This is consistent with the idea that C-S-H is a solid solution containing layers with differing silicate chain lengths, together with interlayer calcium (possibly in the form of layers with the structure of calcium

[†]We use conventional cement chemistry notation, in which C = CaO, S = SiO₂, H = H₂O; the hyphens in C-S-H indicate that it is not a stoichiometric compound, whereas CSH₄ represents CaO•SiO₂•4H₂O.

hydroxide). A simple and rigorous model of growth and dissolution rates of an ideal solid solution has been proposed by Nourtier-Mazauric *et al.*,⁸ which predicts the driving force for, and composition of, the solid that will grow as a function of the aqueous solution composition. If it could be shown to apply to C-S-H, such a model would be particularly useful in reaction-transport models in cementitious systems because it is considerably more computationally efficient than non-ideal solid solution models,^{3,5,9} which may even suffer from numerical instabilities.² Besides this advantage, it is instructive to examine how well an ideal solution model can describe solubility data of C-S-H in comparison to non-ideal solid solution models that require an enthalpy of mixing and therefore more fitting parameters than does the current model. The primary weakness of this simpler ideal solid solution model is that it is not directly tied to the underlying molecular structure of the material, as some more complex non-ideal models have striven to be.³ In particular, the current model does not require any particular composition of the end members, such as one of the tobermorite or jennite minerals that are often used for that purpose.^{3,5,9} Instead, as will be shown, the ideal solid solution model can be fit to determine the compositions of either two or three end members that provide the best agreement with published C-S-H solubility data. Section 3 shows that quite good fits result from end member compositions that are nearly the same as those proposed using some of the most recent thermodynamic and structural models,^{4,6} despite the fact that it assumes zero enthalpy of mixing. Therefore, the current model provides a simple yet accurate and useful new tool for predicting C-S-H composition for use in reaction transport models.

2. Theory

The theory⁸ applies to an ideal solid solution, which means that the free energy of the solid solution differs from that of a physical mixture of the components only as a result of the entropy of mixing. The absence of an enthalpy of mixing is obviously an approximation, but is plausible if the components of the solution have similar crystal structures, as in the C-S-H system. An obvious extension of the model would be to allow for a finite enthalpy of mixing, while retaining an ideal entropy of mixing (*i.e.*, a regular solution model). However, that adds additional parameters and leads to an implicit equation for the composition of the product. Given that excellent fits to experimental measurements are obtained with the ideal solution model, there is no justification for use of the more complicated version.

As outlined in Appendix 1, the theory predicts that the composition of the solid that has the lowest free energy, and is therefore the most favored to grow, is given by

$$\bar{x}_k = \frac{\beta_k}{\sum_{j=1}^N \beta_j}, \quad k = 1, \dots, N \quad (1)$$

where $\bar{x}_k$ is the most favored mole fraction of component k in a solid solution of N components, and the saturation is $\beta_k = Q_k/K_k$, where Q_k is the ion activity product of the aqueous solution and K_k is the equilibrium constant for component k . Therefore, if the

concentrations of the ions in solution and the equilibrium constants for the components are known, then eq. (1) can be used to predict the composition of the solid that precipitates. Appendix 2 shows that the driving force for growth of that compound is the total saturation, β_{Tot} , which is the sum of the saturations of the components:

$$\beta_{Tot} = \sum_{j=1}^N \beta_j \quad (2)$$

This equation has important implications. Suppose that the aqueous solution has a composition identical to the equilibrium activity product for any one component, say $k = 1$ (so $Q_1 = K_1$), then $\beta_1 = 1$; this means that if the solid solution is in equilibrium with the liquid, in which case $\beta_{Tot} = 1$, then eq. (2) requires that the other components are absent (*i.e.*, $\beta_{k \neq 1} = 0$). That is, the solid solution consists of only one component when the activity product in the solution is identical to the equilibrium product for that component. It is sometimes suggested that C-S-H with a high C/S ratio could contain layers with the structure of CH, which would mean that CH could be regarded as a component in the solid solution. This possibility is excluded by eq. (2), because it indicates that C-S-H could not exist in a solution in equilibrium with CH; however, those phases certainly can coexist. This raises two possibilities. Either C-S-H is actually an ideal solid solution that does not contain CH as a component, or C-S-H is a non-ideal solid solution in which CH can be inserted at the price of a positive enthalpy of mixing (see Appendix 1). In the following, we will explore the application of the ideal model, so CH is excluded as a component of the solid solution. Non-ideal solution models of C-S-H have been considered in the past^{5,9,10}, but they are considerably more complicated and not more accurate, at least in terms of mere fitting of published solubility data, than the one presented here.

Suppose that C-S-H is an ideal solid solution of three components with C/S ratios of α_1 , α_2 , and α_3 . The dissolution of each component can be written as

(3)

so the activity product for component k is

$$Q_k = \left\{ \text{Ca}^{2+} \right\}^{\alpha_k} \left\{ \text{H}_3\text{SiO}_4^- \right\} \left\{ \text{OH}^- \right\}^{2\alpha_k - 1} \left\{ \text{H}_2\text{O} \right\}^{n - \alpha_k - 1} \approx \left\{ \text{Ca}^{2+} \right\}^{\alpha_k} \left\{ \text{H}_3\text{SiO}_4^- \right\} \left\{ \text{OH}^- \right\}^{2\alpha_k - 1} \quad (4)$$

where the braces indicate activities; square brackets will be used for molar concentrations. In the absence of significant alkali concentrations like those found in portland cement solutions, the aqueous solutions of calcium and silicate are so dilute that the activity of water is very nearly unity. Even in most portland cement solutions, the mole fraction of water exceeds 0.99, so Raoult's law will apply for water activity and approximating it as unity is still valid. Therefore, water activity will be ignored in the following analysis. We have arbitrarily chosen to write the equilibrium equation in terms of the calcium ion and the monovalent silicate species, H_3SiO_4^- . The equilibrium constant depends on the species chosen to represent equilibrium; the procedure for adjusting the value of the constant according to the choice of species is explained in Appendix 2. However, as explained in Appendix 3, the driving force for growth is independent of the choice of species.

The activity product for calcium hydroxide (CH), Q_{CH} is

$$Q_{CH} = \{\text{Ca}^{2+}\} \{\text{OH}^-\}^2 \quad (5)$$

so eq. (4) can be written as

$$Q_k = Q_{CH}^{\alpha_k} \{\text{H}_3\text{SiO}_4^-\} \{\text{OH}^-\}^{-1} \quad (6)$$

Consequently, the ratio of saturations of any two components is

$$\frac{\beta_j}{\beta_k} = \frac{Q_j K_k}{Q_k K_j} = Q_{CH}^{\alpha_j - \alpha_k} \left(\frac{K_k}{K_j} \right) \quad (7)$$

From eqs. (1) and (7), we find that the mole fractions of components 1 and 2 in the most favored solid solution are given by

$$\bar{x}_1 = \frac{1}{1 + \beta_2/\beta_1 + \beta_3/\beta_1} = \frac{1}{1 + Q_{CH}^{\alpha_2 - \alpha_1} (K_1/K_2) + Q_{CH}^{\alpha_3 - \alpha_1} (K_1/K_3)} \quad (8)$$

$$\bar{x}_2 = \frac{1}{1 + \beta_1/\beta_2 + \beta_3/\beta_2} = \frac{1}{1 + Q_{CH}^{\alpha_1 - \alpha_2} (K_2/K_1) + Q_{CH}^{\alpha_3 - \alpha_2} (K_2/K_3)} \quad (9)$$

and $\bar{x}_3 = 1 - \bar{x}_1 - \bar{x}_2$. The average C/S molar ratio in the solid is

$$\alpha = \sum_{j=1}^N \bar{x}_j \alpha_j = \frac{\alpha_1 K_2 K_3 Q_{CH}^{\alpha_1} + \alpha_2 K_1 K_3 Q_{CH}^{\alpha_2} + \alpha_3 K_1 K_2 Q_{CH}^{\alpha_3}}{K_2 K_3 Q_{CH}^{\alpha_1} + K_1 K_3 Q_{CH}^{\alpha_2} + K_1 K_2 Q_{CH}^{\alpha_3}} \quad (10)$$

The silicate concentration in the aqueous solution does not enter this expression, because it has the same effect on each component of the solid solution. If the solution only contains two components, then the terms involving K_3 are omitted in eqs. (8) – (10).

To find the saturations of the components, β_k , we need to find the equilibrium constant for each component. $\beta_{Tot} = 1$ along the equilibrium solubility curve for C-S-H reported by Chen *et al.*¹. Using eqs. (2) and (4), the condition of equilibrium is

$$1 = \sum_{j=1}^N \frac{Q_j}{K_j} = \sum_{j=1}^N \frac{\{Ca^{2+}\}^{\alpha_j} \{H_3SiO_4^-\} \{OH^-\}^{2\alpha_j-1}}{K_j} \quad (11)$$

Given experimental values for the aqueous solution concentrations of calcium and silicon along the equilibrium curve, we can adjust the values of α_j and/or K_j for the components to obtain the best fit. The activity of species A is related to its molar concentration by the molar activity coefficient γ_A , so $\{A\} = \gamma_A [A]$; the extended Debye-Hückel model will be used to find the molal activity coefficients, γ_A ¹¹, and we assume that $\gamma_A \approx \gamma_A$, because the aqueous solutions under consideration are dilute and have densities very near to that of pure water. The concentration of hydroxyl ions is calculated from the charge balance equation:

$$[OH^-] + [H_3SiO_4^-] + 2[H_2SiO_4^{2-}] = 2[Ca^{2+}] + [CaOH^+] \quad (12)$$

In this equation, it is important to account for the speciation of calcium according to

$$Ca^{2+} + OH^- \rightleftharpoons CaOH^+, \quad K_{Ca} = \frac{\{CaOH^+\}}{\{Ca^{2+}\}\{OH^-\}} = 16.6 \quad (13)$$

and the speciation of silicon according to

$$H_3SiO_4^- + OH^- \rightleftharpoons H_2SiO_4^{2-} + H_2O, \quad K_{Si} = \frac{\{H_2SiO_4^{2-}\}}{\{H_3SiO_4^-\}\{OH^-\}} = 6.76 \quad (14)$$

Since calcium is present in mmol/L concentrations, while silicon is present in $\mu\text{mol/L}$, the impact of silicon on the balance in eq. (12) is negligible. However, its speciation cannot be ignored in the evaluation of eq. (6). Eq. (12) yields pH values only slightly higher than those reported by Haas and Nonat⁴, as shown in Figure 1.

3. Comparison to data

The parameters in the solid solution model were fit to the equilibrium solubility curve for tobermorite-like C-S-H (*i.e.*, Curve A reproduced in Chen *et al.*¹), shown in Figure 2, using a simplex method.¹² Curve A was chosen because, as shown in Figure 2, and despite the high-calcium measurements shown in Chen *et al.*,¹ it is most consistent with the solution compositions observed in the majority of well-hydrated calcium silicate or double-decomposition systems after several weeks, when the C-S-H is likely to be most near equilibrium with the solution. Including data from a few other studies in Figure 10 of Chen *et al.* would produce so much effective scatter in the data at high calcium concentrations that a fit through those data would have dubious value. A set of points of $[\text{Si}]_{\text{meas}}$ versus $[\text{Ca}]$ was taken from Curve A and, for each estimate for the parameters (α_k and K_k), calculated concentrations of silicate, $[\text{Si}]_{\text{calc}}$, were found by satisfying eq. (11) for each value of $[\text{Ca}]$. The residual for each point was defined as $r = 1 - [\text{Si}]_{\text{calc}}/[\text{Si}]_{\text{meas}}$, and the sum of the squared residuals, $\text{SSR} = \sum r^2$, was used to characterize the goodness of fit. Regression analyses were performed by choosing the α_k and fitting the K_k , and by letting all the α_k and K_k be treated as free parameters.

Among the many models in the literature, Stronach and Glasser¹³ chose $(\alpha_1, \alpha_2, \alpha_3) = (0.8, 1.1, 1.8)$ and Blanc *et al.*² chose $(0.8, 1.2, 1.6)$. Haas and Nonat⁴ identified the first two ratios as 0.8 and 1.0, but could not specify the third (expected to be in the range 1.7 to 2). In addition to these combinations, we tested two-component systems with α_1 in the range 0.8 to 1 and with α_2 in the range 1.8 to 2, and (following Richardson⁶), $(2/3, 3/2)$. The initial guesses for K_k were taken from an equation proposed by Blanc *et al.*² to predict the equilibrium constant as a function of α ; their equation was modified to account for our choice of dissolved species, as explained in Appendix 2. Examples of the three-component fits are shown in Figure 3 and the best two-component fits are shown in Figure 4, along with data from some other studies^{14,15,16,17,18}.

The quality of each regression is reported in terms of SSR in Table 1 and Table 2; the last row in each table was obtained by fitting all of the parameters, rather than fixing the α_k . Among the three-component systems, the C/S ratios suggested by Stronach and Glasser performed quite well, but a smaller SSR is obtained with the first two components suggested by Haas and Nonat, together with a third component at $\alpha_3 = 2.0$. If we fix $\alpha_1 = 0.8$ and $\alpha_2 = 1.0$, and leave α_3 as a free parameter along with the K_k , the best-fit value of α_3 is 1.99. Reasonable fits could not be obtained with the C/S ratios suggested by Blanc *et al.*², because the equilibrium constant for $\alpha_2 = 1.2$ became enormous (see Table 1), indicating that that component would be extremely soluble; that is, β_2 would be zero, so the model would effectively reduce to two components with C/S = 0.8 and 1.6. If all six parameters are allowed to vary, the components are found to be $(\alpha_1, \alpha_2, \alpha_3) = (0.88, 1.14, 1.99)$; although these values are close to $(0.9, 1.0, 2.0)$, Table 1 shows that these small shifts in α_k cause

significant changes in the equilibrium constants. Surprisingly, the best fit is obtained with only two components, $\alpha_1 = 0.90$ and $\alpha_2 = 1.96$, with $K_1 = 6.52 \times 10^{-9}$ and $K_2 = 2.86 \times 10^{-15}$.

All of the fits to Curve A shown in Figure 3 and Figure 4 fall within the range of reported experimental data, but there are noticeable differences in the shapes of the curves of C/S versus [Ca]. The parameters giving the best fit to Curve A, Figure 3e and Figure 4e, yield nearly identical curves for C/S, which reach C/S ≈ 1.84 at the point, [Ca] ≈ 20 mmol/L, where the solution is saturated with respect to CH. The curves are closer to the C/S ratios reported by Chen *et al.*¹ and Greenberg and Chang,¹⁷ than to those of Haas and Nonat⁴. Since the calculated values are higher than the expected value of C/S ≈ 1.7 , another set of fits was performed in which the squared residuals gave weight, w , to the departure from the C/S values reported by Haas and Nonat⁴, $(C/S)_{meas}$:

$$SSR = (1 - [Si]_{calc}/[Si]_{meas})^2 + w((C/S)_{meas} - (C/S)_{calc})^2 \quad (15)$$

In these fits, the first components were fixed at $(\alpha_1, \alpha_2) = (0.8, 1.0)$, as suggested by Haas and Nonat, and α_3 was varied along with the K_k . Figure 5 shows, as expected, that the fits to the C/S values move toward the data of ref. 4 at the expense of a slight deterioration in the quality of the fit to Chen's Curve A. As indicated in Table 3, the value of α_3 drops toward 1.75 as w rises, and consequently the predicted C/S ratios decrease. When [Ca] = 20 mmol/L, the predicted C/S values are 1.84 ($w = 0$), 1.66 ($w = 1$), 1.57 ($w = 2$), and 1.54 ($w = 3$). Therefore, the parameters that provide a good fit to Curve A and reasonable values for C/S are obtained with $w = 1$: $(\alpha_1, \alpha_2, \alpha_3) = (0.8, 1.0, 1.8)$. Applying a weighting factor to the fits with two components was less successful, because the C/S versus [Ca] curve becomes strongly sigmoidal; to reduce C/S to 1.7 at [Ca] = 20 mmol/L requires $w = 3$, which results in serious underestimates of C/S at lower [Ca].

The equilibrium constants for the components of the solid solution are compared in Figure 6 to values obtained by Blanc *et al.*², Haas and Nonat⁴, and Damidot and Glasser¹⁹. Based on the scatter in data reported in the literature, Blanc *et al.*² concluded that the uncertainty in $\log_{10}K$ is about ± 0.7 decades. With the exception of one point, the agreement in Figure 6 falls comfortably within those bounds. The line in Figure 6 is a fit to the values from the three-component fit with $w = 1$ and $(\alpha_1, \alpha_2, \alpha_3) = (0.8, 1.0, 1.8)$, and is given by

$$\log_{10}(K_{CSH}) = -2.039 - 6.466\alpha \quad (16)$$

where $\alpha = [Ca]/[Si]$; the correlation coefficient is $R^2 = 0.9975$.

The solid solution model predicts that the individual components of the solid solution are undersaturated while the favored composition grows. Specifically, the saturation of each component is equal to the mole fraction of that component in the favored composition, $\beta_k = \bar{x}_k$. This is illustrated in Figure 7 for the two-component solid solution: along Curve A,

where $\beta_{\text{Tot}} = 1$, each of the components is undersaturated. The solid solution is stabilized by the entropy of mixing, so it can grow under conditions in which its components would dissolve. For example, at the crossover point in Figure 7, the saturation index of each end member is 0.5, and therefore, the mole fraction of each end member is also 0.5. This allows the overall C/S ratio at that point to be calculated as $(0.5 \cdot 0.9) + (0.5 \cdot 1.96) = 1.43$.

The model developed here is intended to describe, and has been compared to measurements on, C-S-H formed from aqueous solutions of calcium and silicate ions, just like most of the existing C-S-H solid solution models of which the authors are aware.^{2,3,5,7,9,10} This makes the current model applicable, for example, to the C-S-H product of tricalcium or dicalcium silicate hydration. In portland cement pastes, other solution components such as alkali cations, aluminates, sulfates, and carbonates can be accommodated in C-S-H,^{4,6,13,19} and consequently the current model is not strictly applicable to C-S-H in portland cement systems. Even so, this model may still provide a good approximation of C/S ratios even in those cases. In addition, the model could be readily extended in the future to include stoichiometric end members that contain one or more of these other components and compared to solid solution models of, for example, C-(A)-S-H.⁴

4. Conclusions

The solid solution model with either two or three components provides fits to reported solubility curves for C-S-H that are well within the scatter in the data, and also yields predictions of the calcium/silicon molar ratio in the C-S-H that precipitates from a given solution that are consistent with experimental measurements. The best fits to the solubility curve were obtained with three components having C/S ratios of $(a_1, a_2, a_3) = (0.9, 1.39, 1.93)$, or with two components having ratios of $(a_1, a_2) = (0.9, 1.96)$. Comparable results are obtained with $(a_1, a_2, a_3) = (0.8, 1, 2)$, which has the advantage that the first two components have compositions that agree with the best thermodynamic data^{4,7}. However, those parameters yield values of the C/S ratio in the C-S-H that are higher than is generally reported. When the fits are forced to approach the C/S ratios reported in ref. [4], satisfactory fits are obtained with $(a_1, a_2, a_3) = (0.8, 1.0, 1.8)$. The equilibrium constants for the end-members of the solid solution are in good agreement with data from the literature^{2,4,19}. The three-component model suggested by Stronach and Glasser¹³ (0.8, 1.1, 1.8) also performs well, but the set suggested by Blanc *et al.*² (0.8, 1.2, 1.6) leads to an unreasonable value for the equilibrium constant of the middle component.

This solid solution model has been examined primarily to determine whether it can provide sufficiently accurate predictions of C-S-H solubility to justify it as a numerically stable efficient alternative to its non-ideal counterparts for reaction transport modeling. However, the fact that the best fits of the ideal model to solubility data are obtained with end member compositions very near those of the most recent C-S-H thermodynamic studies suggests that the model may be more than just an expedient tool for hydration simulations. Besides being easy to implement, it readily predicts both the composition of the solid with the greatest driving force for growth, as well as the driving force for dissolution of thermodynamically unfavorable compositions, given the concentrations of species in the aqueous solution. Furthermore, as shown in the Appendix, generalizing the model to that of a regular solid

solution with constant enthalpy of mixing is straightforward. Such a generalization would enable the inclusion of portlandite as an end member, which may be necessary to explain some of the higher C/S ratios that have been reported in solutions with very high calcium concentrations.⁶

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Appendix 1. Solid solution theory

Following Nourtier-Mazauric *et al.*⁸, we consider an ideal solid solution with N components (or, end-members) E_k ($k = 1, \dots, N$); the composition of the solid solution is specified by the mole fractions of the components, x_k . The dissolution of a solid solution with a particular composition, $(\bar{x}_1, \dots, \bar{x}_N)$, can be separated into two steps: (1) unmixing of the solution into its pure components, then (2) dissociation of the components into their solution species. The first step is

$$SS \rightarrow \bar{x}_1 E_1 + \dots + \bar{x}_N E_N, \quad \Delta G_m = -RT \sum_{j=1}^N (\bar{x}_j \ln (\bar{x}_j)) \quad (17)$$

The free energy change, G_m , is the ideal entropy of *unmixing* (so it is positive); there is no enthalpic contribution for an ideal solution. The second step for each component is

$$\bar{x}_k E_k \rightarrow \bar{x}_k \sum_{j=1}^{N_k} (n_{k,j} e_{k,j}), \quad \Delta G_k = \bar{x}_k (\Delta G_k^0 + RT \ln (Q_k)) \quad (18)$$

where $e_{k,j}$ is the j th species in the k th component, E_k , $n_{k,j}$ is its stoichiometric coefficient, and N_k is the number of species appearing in component k ; ΔG_k^0 is the standard free energy of dissolution,

$$\Delta G_k^0 = -RT \ln (K_k) \quad (19)$$

where K_k is the equilibrium constant for component k , and the activity product is

$$Q_k = \prod_{j=1}^{N_k} \{e_{k,j}\}^{n_{k,j}} \quad (20)$$

where the braces indicate the activity of species $e_{k,j}$. Adding the reactions,

$$SS \rightarrow \sum_{k=1}^N \bar{x}_k E_k = \sum_{k=1}^N \bar{x}_k \sum_{j=1}^{N_k} (n_{k,j} e_{k,j}) \quad (21)$$

we find that the free energy change upon dissolution is

$$\frac{\Delta G_{diss}}{RT} = \sum_{j=1}^N \left(\bar{x}_j \ln \left(\frac{Q_j}{K_j} \right) - \bar{x}_j \ln (\bar{x}_j) \right) = \sum_{j=1}^N \left(\bar{x}_j \ln \left(\frac{\beta_j}{\bar{x}_j} \right) \right) = \ln \left(\prod_{j=1}^N \left(\frac{\beta_j}{\bar{x}_j} \right)^{\bar{x}_j} \right) \quad (22)$$

where the saturation of component k is defined as $\beta_k = Q_k/K_k$. The argument in the last term of eq. (22) is called the stoichiometric saturation, Ω_{SS} :

$$\Omega_{SS} \equiv \prod_{j=1}^N \left(\frac{\beta_j}{\bar{x}_j} \right)^{\bar{x}_j} \quad (23)$$

When this quantity is unity, the solid is at equilibrium with the aqueous solution and $G_{diss} = 0$. This indicates that $\beta_k = \bar{x}_k$ at equilibrium, so each component of the solid solution is undersaturated and would tend to dissolve; however, the solid solution is stable because it benefits from the entropy of mixing.

In the presence of a given aqueous solution, there is a particular solid solution that has the highest (least negative) value of G_{diss} , so it is the one that is favored to precipitate. At the extremum, the derivative of G_{diss} with respect to each $\bar{x}_k$ must be zero. Since the sum of the mole fractions is unity, only $N-1$ of them are independent. If we rewrite eq. (22) as

$$\frac{\Delta G_{diss}}{RT} = \sum_{j=1}^{N-1} \left(\bar{x}_j \ln (\beta_j) - \bar{x}_j \ln (\bar{x}_j) \right) + \left(1 - \sum_{j=1}^{N-1} \bar{x}_j \right) \left(\ln (\beta_N) - \ln \left(1 - \sum_{j=1}^{N-1} \bar{x}_j \right) \right) \quad (24)$$

and take the derivative with respect to any $\bar{x}_j$ we obtain

$$\frac{\partial}{\partial \bar{x}_j} \left(\frac{\Delta G_{diss}}{RT} \right) = \ln \left(\frac{\beta_j}{\bar{x}_j} \right) - 1 - \ln (\beta_N) + \ln \left(1 - \sum_{j=1}^{N-1} \bar{x}_j \right) + 1 = \ln \left(\frac{\beta_j \bar{x}_N}{\bar{x}_j \beta_N} \right) = 0 \quad (25)$$

The final equality means that

$$\bar{x}_N \beta_j = \bar{x}_j \beta_N \quad (26)$$

Summing both sides over j from 1 to N , we find that

$$\bar{x}_N = \frac{\beta_N}{\sum_{j=1}^N \beta_j} = \frac{\beta_N}{\beta_{Tot}} \quad (27)$$

where the total saturation, β_{Tot} , is the sum of the saturations of the components. Since we chose the N th component arbitrarily, eq. (27) yields the mole fraction for every component of the favored composition of the solid solution. The driving force for the growth of that composition can be found by substituting eq. (27), with subscript N replaced by j , into eq. (23):

$$\Omega_{SS} = \prod_{j=1}^N (\beta_{Tot})^{\beta_j / \beta_{Tot}} = (\beta_{Tot})^{\sum_{j=1}^N \beta_j / \beta_{Tot}} = \beta_{Tot} \quad (28)$$

Thus, the total saturation is the driving force for growth of the preferred composition.

Suppose that the solid solution is *not* ideal, because there is a nonzero enthalpy of mixing, H_{mix} , which is a function of composition. In that case, the unmixing energy in eq. (17) is replaced by

$$\Delta G_m = - \left(\Delta H_{mix} + RT \sum_{j=1}^N (\bar{x}_j \ln (\bar{x}_j)) \right) \quad (29)$$

where the sign is chosen so that mixing in the solid solution is favored when $H_{mix} < 0$. Proceeding as before, the free energy of dissolution is

$$\frac{\Delta G_{diss}}{RT} = \ln \left(\prod_{j=1}^N \left(\frac{\beta_j}{\bar{x}_j} \right)^{\bar{x}_j} \right) - \frac{\Delta H_{mix}}{RT} \equiv \ln (\Omega_{SS}) \quad (30)$$

and eq. (23) is replaced by

$$\Omega_{SS} = \exp\left(-\frac{\Delta H_{mix}}{RT}\right) \prod_{j=1}^N \left(\frac{\beta_j}{\bar{x}_j}\right)^{\bar{x}_j} \quad (31)$$

Thus, the more negative the heat of mixing, the greater the supersaturation of the solid solution at a given concentration in the aqueous solution, which means that a negative heat of mixing favors growth. Since equilibrium requires $\Omega_{SS} = 1$, eq. (31) requires that $\beta_k < \bar{x}_k$ when $H_{mix} < 0$ (because the heat of mixing further stabilizes the solid solution), and $\beta_k > \bar{x}_k$ when $H_{mix} > 0$. Therefore, even if one of the components is in equilibrium, say $\beta_1 = 1$, it is still true that $x_1 < 1$. This means that it would be possible to have a solid solution with CH as a component, which could co-exist with a saturated solution of CH, if the heat of mixing for CH is positive.

Appendix 2. Adjustment of equilibrium constants

Blanc *et al.*², as well as Haas and Nonat⁴, write the dissolution of C-S-H in terms of the neutral silicate species (fully protonated silicic acid), in the form

so the equilibrium constant has the form

$$K_{CSH}^B = \frac{\{\text{Ca}^{2+}\}^\alpha \{\text{H}_4\text{SiO}_4\}}{\{\text{H}^+\}^{2\alpha}} \quad (33)$$

whereas we prefer to write the dissolution in terms of the monovalent silicate species,

for which

$$K_{CSH} = \{\text{Ca}^{2+}\}^\alpha \{\text{H}_3\text{SiO}_4^-\} \{\text{OH}^-\}^{2\alpha - 1} \quad (35)$$

To relate this quantity to that reported by Blanc *et al.*, we must take account of the following equilibria:

Using eq. (33) to write $\{\text{Ca}^{2+}\}$ in terms of K_{CSH}^B , we find

$$\begin{aligned} K_{CSH} &= \frac{K_{CSH}^B \{\text{H}^+\}^{2\alpha}}{\{\text{H}_4\text{SiO}_4\}} \{\text{H}_3\text{SiO}_4^-\} \{\text{OH}^-\}^{2\alpha-1} = K_{CSH}^B \left(\frac{\{\text{H}_3\text{SiO}_4^-\}}{\{\text{H}_3\text{SiO}_4\}\{\text{OH}^-\}} \right) (\{\text{OH}^-\}\{\text{H}^+\})^{2\alpha} \\ &= K_{CSH}^B K_{Si} K_H^{2\alpha-1} = K_{CSH}^B \times 10^{4.19-28\alpha} \end{aligned} \quad (38)$$

Appendix 3. Driving force for growth

The equilibrium equation can be written in terms of the monovalent silicate ion,

or the divalent form,

If the silicate species are in equilibrium with each other, then their activities are related by eq. (14), and the respective equilibrium constants for reactions (39) and (40), K_I and K_{II} , are related by

$$K_{II} = K_I K_{eq}^{Si} \quad (41)$$

The saturations for reactions (39) and (40) are

$$\beta_I = \frac{\{\text{Ca}^{2+}\}^\alpha \{\text{H}_3\text{SiO}_4^-\} \{\text{OH}^-\}^{2\alpha-1}}{K_I} \quad (42)$$

and

$$\beta_{II} = \frac{\{\text{Ca}^{2+}\}^\alpha \{\text{H}_2\text{SiO}_4^{2-}\} \{\text{OH}^-\}^{2\alpha-2}}{K_{II}} \quad (43)$$

According to eq. (14), we can write

$$\frac{\{\text{H}_2\text{SiO}_4^{2-}\}}{K_{eq}^{Si}} = \{\text{H}_3\text{SiO}_4^-\} \{\text{OH}^-\} \quad (44)$$

so eq. (43) can be written as

$$\beta_{II} = \frac{\{\text{Ca}^{2+}\}^\alpha \{\text{H}_2\text{SiO}_4^{2-}\} \{\text{OH}^-\}^{2\alpha-2}}{K_I K_{eq}^{Si}} = \frac{\{\text{Ca}^{2+}\}^\alpha \{\text{H}_3\text{SiO}_4^-\} \{\text{OH}^-\}^{2\alpha-1}}{K_I} = \beta_I \quad (45)$$

Thus, the driving force for growth is the same for each species. A similar argument would apply for any other species, such as Ca^{2+} and CaOH^+ .

The mono- and divalent species might have different rates of attachment to a growing crystal of C-S-H, so the growth rate of each species can be written as

$$G_k = G_{0k} (\beta_k^{1/m} - 1)^n, k = I, II \quad (46)$$

where G_{0k} is a constant specific to the ionic species, and m and n are constants related to the mechanism of growth. The observed growth rate, G , will be the sum of the rates contributed by each species, so taking account of eqs. (45) and (46),

$$G = G_I + G_{II} = G_0 (\beta_I^{1/m} - 1)^n = G_0 (\beta_{II}^{1/m} - 1)^n \quad (47)$$

where $G_0 = G_{0I} + G_{0II}$. Thus, the growth rate can be written in terms of the supersaturation of either species with the same rate constant, G_0 , as long as the growth mechanism (characterized by m and n) is the same for each.

Figure 1. pH versus calcium concentration. Symbols are the measured and calculated values from Haas and Nonat [4]; curves calculated with optimal parameters for two- and three-component systems. The dashed curve is nearly coincident with the solid curve and is therefore difficult to observe.

Figure 2.

Curve A as drawn by Chen et al. [1] (solid curve), with data (symbols) from Taylor [16], Fuji and Kondo [15], Greenberg and Chang [17], and Brown et al. [14].

Figure 3.

In plots a, c, and e, the red dots are points from Curve A of Chen et al. [1] that were used for fitting, and the curves are the fits; the curves in plots b, d, and f were calculated based on the fits. (a) Fit to Curve A and (b) calculated C/S versus $[Ca]$ using $(a_1, a_2, a_3) = (0.8, 1.1, 1.8)$; (c) Fit to Curve A and (d) calculated C/S versus $[Ca]$ using $(a_1, a_2, a_3) = (0.8, 1.0, 2.0)$; (e) Fit to Curve A and (f) calculated C/S versus $[Ca]$ using $(a_1, a_2, a_3) = (0.88, 1.14, 1.99)$. Symbols are experimental data: in (a,c,e) inverted triangles = Brown et al. [14], triangles = Fuji and Kondo [15], squares = Taylor [16], diamonds = Haas and Nonat [4]; in (b,d,f) red circles = Haas and Nonat [4], triangles = Nonat and Lecoq [18], squares = Greenberg and Chang [17], diamonds = Chen et al. [1].

Figure 4.

In plots a, c, and e, the red dots are points from Curve A of Chen et al. [1] that were used for fitting, and the curves are the fits; the curves in plots b, d, and f were calculated based on the fits. (a) Fit to Curve A and (b) calculated C/S versus $[Ca]$ using $(a_1, a_2) = (2/3, 3/2)$; (c) Fit to Curve A and (d) calculated C/S versus $[Ca]$ using $(a_1, a_2) = (0.8, 1.8)$; (e) Fit to Curve A and (f) calculated C/S versus $[Ca]$ using $(a_1, a_2) = (0.9, 1.96)$. Symbols identified in Figure 3.

Figure 5.

Combined fits (solid curves) to Curve A of Chen et al. [1] (red dots in a,c,e) and the C/S data of Haas and Nonat [4] (red dots in b,d,f). The first two components were fixed at $(a_1, a_2) = (0.8, 1.)$, while a_3 and the K_k were varied. The weighting factor in eq. (15) is $w = 1$ in (a,b), $w = 2$ in (c,d), and $w = 3$ in (e,f). Symbols are identified in Figure 3.

Figure 6.

Logarithm of equilibrium constant versus C/S from Blanc et al. [2] (B); Damidot and Glasser [19] (D&G), and Haas and Nonat [4] (H&N), and the end-members of the solid solution with $(a_1, a_2) = (0.9, 1.96)$ (2-comp), $(a_1, a_2, a_3) = (0.88, 1.14, 1.99)$, and $(a_1, a_2, a_3) = (0.8, 1.0, 1.8)$ (3-comp $w = 1$) components; line is a least-squares fit to the latter curve.

Figure 7.
Saturation of each component of the optimal two-component solid solution $(\alpha_1, \alpha_2) = (0.90, 1.96)$.

Table 1

The goodness of fit of eq. (11) to Curve A using three components, reported as the sum of squared residuals (SSR). The α_k were prescribed except in the last line, where the α_k were fit along with the K_k .

Ref. ^a	α_1	α_2	α_3	SSR	$K_1 \times 10^8$	$K_2 \times 10^{10}$	$K_3 \times 10^{14}$
13	0.8	1.1	1.8	0.050	5.11	14.76	2.35
4 ^b	0.8	1.0	1.8	0.044	5.82	49.7	2.33
4 ^b	0.8	1.0	1.9	0.018	7.30	28.2	0.729
4 ^b	0.8	1.0	2.0	0.017	9.18	20.9	0.227
2	0.8	1.2	1.6	0.236	5.00	4.99×10^9	24.8
6 ^c	2/3	3/2	1.8	0.238	54.8	0.0156	4.13
6 ^c	2/3	3/2	2.0	0.204	55.6	0.0124	0.498
Optimal	0.90	1.39	1.93	0.013	0.742	3.48	0.511

^aReference to paper in which 2 or 3 of these α_k were proposed

^bHaas and Nonat identified ratios 0.8 and 1.0

^cRichardson identified ratios 2/3 and 3/2

Table 2

The goodness of fit of eq. (11) to Curve A using two components, reported as the sum of squared residuals (SSR). The α_k were prescribed except in the last line, where the α_k were fit along with the K_k .

α_1	α_2	SSR	$K_1 \times 10^8$	$K_2 \times 10^{14}$
2/3	3/2	0.434	64.3	79.2
0.8	1.8	0.0846	4.27	2.18
0.8	2.0	0.317	3.66	0.192
0.9	1.9	0.0154	0.699	0.723
0.9	2.0	0.0262	0.671	0.217
1.0	2.0	0.215	0.116	0.260
0.90	1.92	0.0126	0.727	0.537

Table 3

Results of combined fits to Curve A [1] and C/S [4]

w	α_1	α_2	α_3	SSR	$K_1 \times 10^8$	$K_2 \times 10^9$	$K_3 \times 10^{14}$
0	0.8	1.0	1.96	0.0145*	8.27	2.35	0.384
1	0.8	1.0	1.81	0.621	14.3	1.59	2.47
2	0.8	1.0	1.82	1.12	7.35	1.84	2.23
3	0.8	1.0	1.83	1.32	8.66	1.41	2.32

* This value cannot be compared to the others in this table, because the departure from the C/S data is not included.