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A model for dissolution of $CaO-SiO_2-H_2O$ gel at $Ca/Si > 1$

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Abstract

Calcium silicate hydrate ($CaO-SiO_2-H_2O$) gel is the principal hydration product of Portland cement. Experimental data show that the dissolution of $CaO-SiO_2-H_2O$ (C-S-H) gel is strongly dependent on Ca/Si (C/S) ratio in the range of $C/S > 1$. A model for dissolution of C-S-H gel is presented by considering a nonideal mixture of binary solid solutions of Margules type. Guggenheim and Prausnitz equations are applied to represent the activities of model solids as a function of mole fractions. The Gibbs-Duhem equation, incorporating the activities of model solids, is then used to express the conditional solubility products of model solids in terms of C/S ratio. The determination of Guggenheim's empirical parameters is performed with geochemical code PHREEQE on experimental data. By these procedures, a dissolution model of C-S-H gel is described. The solubility results predicted by the proposed model are comparable with experimental data.

Keywords: C-S-H gel; Margules type solid; Dissolution; Conditional solubility product

Safe disposal of radioactive wastes in the geological environment is a challenging task. Because the time period involved in geological disposal extends well beyond the normal horizon of human activities, it is not possible to demonstrate directly the safety assessment of the disposal system for its intended lifetime. The long-term safety can only be predicted by means of a series of predictive calculations on the behavior of multibarrier systems of the repository. Cementitious materials are commonly used in the multibarrier systems of low and transuranic radioactive waste repositories. The chemical reaction of cement with water develops high pH, which has beneficial effects on the immobilization and low solubility of radionuclides such as actinides. The good sorption properties of cement for many radionuclides constitute an important factor in delaying and decreasing their release into the environment. During degradation, the hydrated cement will dissolve in the intruding groundwater. Calcium silicate hydrate (C-S-H) gel is the principal hydration product of cement. Other cement phases such as ettringite ($Ca_6Al_2O_6(SO_4)_3 \cdot 32H_2O$), monosulfate ($Ca_4Al_2O_6SO_4 \cdot 12H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), hydrogarnet ($Ca_3Al_2(OH)_{12}$), and others are also important in hydrated cement [1,2].

In order to elucidate the immobilization of radionuclides, it is necessary to describe the long-term dissolution behavior of these phases. The dissolution behavior of C-S-H gel is complex compared with other phases. The dissolution of C-S-H gel is incongruent in the compositional range $0.8–1 < C/S \leqslant 1.4–1.5$ with Ca_{total} concentrations being much higher than those of Si_{total} in solution [3–8]. Moreover, the extent of the incongruent dissolution of C-S-H gel gradually increases with the C/S ratio, which has a major impact on the safety assessment of radioactive waste disposal. There are many experimental reports published for the C-S-H gel system [3–8]. The data from these reports cannot be used directly for the long-term safety assessment of radioactive waste disposal because of the short time period involved in these experiments. In addition, there are some relative inconsistencies in these experimental results [9]. On the other hand, there is no clear evidence of the long-term chemical behavior of C-S-H gel can be used in the long-term safety assessment of the repository. In order to describe the long-term dissolution of C-S-H gel, it is necessary to develop mathematical expressions by comparing with experimental data for the safety assessment of radioactive wastes disposal.

Several thermodynamic models have been proposed to model the incongruent dissolution behavior of C-S-H gel [2,10–13]. Berner [10] proposed a model derived by extracting thermodynamic expressions for the solubility products of model solids in which nonconstant solubility products are used as fitting parameters to describe experimental data in the C-S-H gel system. In the Berner model, calculated Ca_{total} concentrations in solution are higher than those of experimental data in the C/S ratio between 1 to 1.25.

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Borjesson et al. [12] suggested a thermodynamic model by considering the activity of a model solid of Margules type, indicating that a calcium-rich gel coexists with almost pure $Ca(OH)_2(s)$ in the region $C/S > 1.43$. In their model, Ca_{total} concentrations in solution agree well with the experimental data However, Si_{total} and pH values in solution are not reported. In previous models [2,10–13], the dissolution behavior of C-S-H gel (e.g., Ca_{total}, Si_{total}) and pH values are not reported completely by considering Margules type of solid solutions. In addition, the phase transitions in the C-S-H gel are not taken into account.

The available information [14,15] indicates that C-S-H gel has a layer structure containing calcium silicate sheets in solid solution with $Ca(OH)_2$ and H_2O. The C/S ratio in the C-S-H gel is known to cover the range between 0.7 to approximately 2.0. In this range, Taylor [16] proposed two different types of C-S-H gel, namely C-S-H (I) and C-S-H (II). The phase transition between these two C-S-H gels occurs at $C/S = 1.5$. Within the compositional range of C-S-H (I) ($C/S = 0.7$–1.5), it is reported that a second phase transition occurs at $C/S = 1$ [17,18]. Recent studies by nuclear magnetic resonance spectroscopy confirm that three kinds of C-S-H [C-S-H(α) for C/S below 1, C-S-H(β) for C/S between 1 and 1.5, and C-S-H(γ) for C/S over 1.5] exist in the hydrate cement phases [19,20]. The variation of C/S ratio in the C-S-H gel mainly occurs due to the variation of silicate-chain length and insertion in interlayer positions of calcium ions balancing silicate and hydroxide negative charges. In C-S-H(β), the C/S increase is mainly due to elimination of bridging tetrahedra and insertion of calcium ions balancing SiO^- charges; in C-S-H(γ), it is due to insertion of calcium ions balancing OH^-, which may be localized in the structure in place of missing bridging silicates. The interlayer calcium ions are bonded to the end-chain tetrahedra (Q_{1ca}) in this region. In C-S-H(γ), C-S-H with C/S greater than 1.5 could be considered as a solid solution of portlandite (CH) and C-S-H gel. Therefore, the dissolution of the hydrate cement phases can be described by introducing phase transitions in the C-S-H gel. In this study, a dissolution model of C-S-H gel is proposed by assuming Margules-type solid solutions at $C/S > 1$. The mathematical expressions for the dissolution of C-S-H gel are presented and compared with experimental data. The phase transition at $C/S = 1.5$ is considered for the boundary between C-S-H(β) and C-S-H(γ). By assuming these, a dissolution model of C-S-H gel is developed for the safety assessment of radioactive waste disposal.

1. End members of the C-S-H gel as model solids

Greenberg and Chang [3] considered from their experimental data in the C-S-H gel system that several solid phases exists in the system, depending on C/S ratio at 25°C: (1) silica and silica partially reacted with $Ca(OH)_2$ at $C/S < 0.14$; (2) partially reacted silica and CaH_2SiO_4 at $0.14 < C/S < 1$; (3) CaH_2SiO_4 with varying amounts of $Ca(OH)_2$ at $1 < C/S < 1.75$; and (4) $CaH_2SiO_4 \cdot n\, Ca(OH)_2$ and $Ca(OH)_2$ at $C/S > 1.75$. Berner [10] has proposed a thermodynamic model with a nonideal mixture of binary solid solutions: (1) at $0 < C/S \leqslant 1$, SiO_2 and CaH_2SiO_4; (2) at $1 < C/S \leqslant 2.5$, $Ca(OH)_2$ and CaH_2SiO_4; and (3) at $C/S > 2.5$, $Ca(OH)_2$ and CaH_2SiO_4. Considerations of model solids such as $Ca(OH)_2$ and CaH_2SiO_4 in both ranges (1) and (3) are identical in the Berner model. But numerical values for the solubility products of these solids are different in ranges (2) and (3). For example, the solubility product of $Ca(OH)_2$ is assumed to be dependent on C/S ratio in the range (2), while the solubility product of CaH_2SiO_4 is assumed to be constant in this range. In range (3), the solubility products of these model solids are assumed to be constant values in the Berner model. Borjesson et al. [12] constructed a model with $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$ in the region $C/S > 1$ and concluded that phase separation occurs at the $C/S = 1.43$, at which composition the activity of the end-member $Ca(OH)_2(s)$ is unity.

In the present model, we consider a two solid-phase system by assuming Margules-type solid solutions. We assume a nonideal mixture of solid solutions of $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$ in the region $1 < C/S \leqslant 1.5$, while $Ca(OH)_2(s)$ is considered to coexist with C-S-H gel at $C/S > 1.5$. At $C/S > 1.5$, the C-S-H gel is represented by the end-members $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$. The end-member $Ca(OH)_2(s)$ exists as almost pure solid in this region. Due to the strong incongruent dissolution behavior of C-S-H gel at $1 < C/S \leqslant 1.5$ [3–8], we assume conditional solubility products of $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$ in this range. Here the term “conditional solubility product” means the solubility product of a solid that depends on C/S ratio. The conditional solubility product of $Ca(OH)_2(s)$ is assumed as a constant value over $C/S > 1.5$ due to the saturation concentration of Ca_{total} in solution for portlandite. The phase transition at $C/S = 1.5$ is in accord with recent studies [16–20]. It can be seen from the experimental data [3–6,8] that Si_{total} concentrations in solution are very low and scattered at $C/S > 1.5$. Therefore in our model the conditional solubility product of $CaH_2SiO_4(s)$ is arbitrary, and we considered it to have a constant value at $C/S > 1.5$.

2. Dissolution model

The C-S-H gel consists of a nonideal mixture of solid solutions. The activity of a nonideal solid solution is related to its mole fraction. The chemical potential of a nonideal solid solution of ith component at a given temperature and pressure is given by Eq. (1):

$$\mu_i = \mu_i^0 + RT \ln x_i \gamma_i \tag{1}$$

where μ_i and μ_i^0 are the chemical and standard potential of the component i, respectively; x_i and γ_i are the mole fraction and activity coefficient of the component i, respectively; T is the temperature in Kelvins and R the gas constant. In order to use Eq. (1), the activity coefficient of the component i

must be evaluated accurately. These are related to the excess free energy of a nonideal solid solution of component *i* [21] as shown in Eq. (2):

$$G_{\text{excess}} = RT\sum_i x_i \ln\gamma_i \tag{2}$$

where G_{excess} is defined by the excess free energy between the enthalpy of the nonideal solid solution and that of the ideal solid solution. In this study, we use an empirical formulation of the Margules type where G_{excess} can be expressed with a power series of the mole fractions of components. This type of polynomial expansion is used extensively to describe the deviations from ideality in solid solutions consisting of two and three components [22]. For a nonideal mixture of binary solid solutions of Margules type, the mixing model proposed by Guggenheim [see 23–25] is applied to describe the incongruent dissolution behavior of C-S-H gel. For a binary nonideal solid solution this expression becomes [Eq. (3)]

$$G_{\text{excess}} = x_1x_2[A_0 + A_1(x_1 - x_2)] \tag{3}$$

where the parameters A_0 and A_1 are not dependent on composition but on temperature and pressure. The activity coefficient of the end-member *i* can be described as a function of the composition given by Prausnitz [21] as Eq. (4):

$$RT\ln\gamma_1 = \left(\frac{\partial n_T G_{\text{excess}}}{\partial n_i}\right)_{T,P,ni} \tag{4}$$

where n_i is the number of moles of end-member *i* and n_T the total number of moles. The derivative used in Eq. (4) is taken at constant temperature, pressure, and number of moles of all other end-members except *i*. Using the relation $a_i = x_i\gamma_i$ with Eqs. (2) to (4), the activities of the end-members for $Ca(OH)_2(s)$ can be expressed as Eq. (5):

$$a_1 = x_1\exp[x_2^2\{\alpha_0 + \alpha_1(3x_1 - x_2)\}] \tag{5}$$

and for $CaH_2SiO_4(s)$ can be expressed as Eq. (6):

$$a_2 = x_2\exp[x_1^2\{\alpha_0 - \alpha_1(3x_2 - x_1)\}] \tag{6}$$

The dimensionless empirical parameters α_0 and α_1 are expressed by A_0/RT and A_1/RT, respectively.

The dissolution of the particular components can be described by using the concept of variable activities in the solid state. The Gibbs-Duhem equation for the nonideal mixture of two solids gives a relation between the activities of the components in the solid state [Eq. (7)]:

$$\ln a_1^{(s)} = -\frac{x_2}{x_1}\cdot\ln a_2^{(s)} + C \tag{7}$$

where C is an integration constant depending on x_1 and x_2. $a_i^{(s)}$ is the activity of component *i* in the solid state. The solid state activity of a single solid can be expressed as shown in Eq. (8)

$$\ln a_i^{(s)} = -\ln K_{so}^i + \ln a_i^{(l)},\ (i = 1{,}2) \tag{8}$$

where $a_i^{(l)}$ is the activity in the dissolved state and K^i_{SO} is the solubility product of the pure model solid *i*. The terms $\ln a_i^{(s)}$ and $\ln a_i^{(l)}$ in Eq. (8) depend on the composition of the mixture and Eq. (8) can be written as Eq. (9):

$$\begin{aligned}\log a_i^{(l)}(\text{C/S}) &= \log a_i^s(\text{C/S}) + \log K_{so}^i\\ &= \log K_{so}^i(\text{C/S})\end{aligned} \tag{9}$$

Using Eqs. (5) to (9), conditional solubility products of $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$ can be written as a function of activities and mole fractions of model solids as shown in Eq. (10) and Eq. (11):

$$\log K_{so}^1(\text{C/S}) = C' + \log K_{so}^1 - \frac{x_2}{x_1}\log a_2^{(s)} \tag{10}$$

$$\log K_{so}^2(\text{C/S}) = \log K_{so}^2 + \frac{x_1}{x_2}(C' - \log a_1^{(s)}) \tag{11}$$

where the integration constant C' is expressed as $C' = \log a_1^{(s)} - (1 - 1/x_1)\log a_2^{(s)}$. K^1_{SO} and K^2_{SO} are the solubility products of pure model solids of $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$, respectively, considered as constant values. The $\log K^1_{SO}$(C/S) and $\log K^2_{SO}$(C/S) are conditional solubility products of nonideal mixture of $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$, respectively, depending on C/S ratio in the region $1 < \text{C/S} \leqslant 1.5$. The integration constant C' is defined by the mole fraction x_1 with $a_1^{(s)}$ and $a_2^{(s)}$. Therefore, C' is taken as a function of mole fractions or of C/S ratio.

Using Eqs. (5) to (11), conditional solubility products of $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$ can be represented as a function of C/S ratio, as seen in Eq. (12) and Eq. (13)

$$\log K_{so}^1(\text{C/S}) = C' + \log K_{so}^1 - \frac{1}{\text{C/S}-1}\left\{\frac{1}{2.3}\left(\frac{\text{C/S}-1}{\text{C/S}}\right)^2\left[\alpha_0 - \alpha_1\left(\frac{4-\text{C/S}}{\text{C/S}}\right)\right] + \log\frac{1}{\text{C/S}}\right\} \tag{12}$$

$$\log K_{so}^2(\text{C/S}) = C'(\text{C/S}-1) + \log K_{so}^2 - (\text{C/S}-1)\left\{\frac{1}{2.3}\left(\frac{1}{\text{C/S}}\right)^2\left[\alpha_0 + \alpha_1\left(\frac{3\text{C/S}-4}{\text{C/S}}\right)\right] + \log\left(\frac{\text{C/S}-1}{\text{C/S}}\right)\right\} \tag{13}$$

where x_1 and x_2 are replaced by (C/S − 1)/(C/S) and 1/(C/S), respectively. Since the solubility product of pure solid is considered as a fixed value, the values of $\log K^1_{SO}$(C/S) (=−5.15) and $\log K^2_{SO}$(C/S) (=−8.16) are taken from the literature [26,27]. Eqs. (12) and (13) are expressed to define conditional solubility products of $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$, respectively, in region $1 < \text{C/S} \leqslant 1.5$.

3. Results and discussion

3.1. Determinations of empirical parameters

The dimensionless empirical parameters α_0 and α_1 in Eqs. (5) and (6) can be determined from experimental data. Saturation indices (SI_i) can be used to obtain the activity of model solids from experimental data at a specific C/S ratio. The saturation indices are used to describe the apparent closeness to equilibrium between a solid phase and an aqueous solution [27]. For solid dissolution reactions, saturation indices can be formulated as shown in Eq. (14)

$$SI_i = \log\frac{IAP_i}{K_{so}^i} \tag{14}$$

where IAP_i is the ion activity product of the end-member *i*. A log *SI* value of zero indicates that water is saturated with respect to a particular solid and a value less than zero means it is undersaturated. In other words, a saturated solution exists only when the ion activity product (IAP_i) of the dissolved ions is exactly equal to K^i_{SO}. Usually, an ion activity product describes whether precipitation will occur in the solution or not. The activity of the end-member *i* in a solid solution with an aqueous phase in equilibrium becomes [see Eq. (15)] [12]

$$a_i^{\text{Solid solution}} = \frac{IAP_i}{K_{so}^i} \tag{15}$$

Combining Eq. (14) with Eq. (15), the activity of the end-member *i* becomes [see Eq. (16)]

$$a_i^{\text{Solid solution}} = 10^{SI_i} \tag{16}$$

The experimental data reported elsewhere [3–6,8] are used with geochemical code PHREEQE to obtain SI_i values for various C/S ratios. Not all these experimental data can be used to model the dissolution of C-S-H gel because of different temperature, experimental procedure, and ionic strength correction used in these experiments. Since the main purpose of this study is to develop mathematical expressions for the dissolution of C-S-H gel by comparing with experimental data for the safety assessment of radioactive waste disposal, we assume that temperature difference and different ionic strength correction have little effect on the safety assessment of radioactive waste disposal. In the Geochemical code PHREEQE, we use the databases of MINEQL [26]; PHREEQE [27], and CHEMVAL6 [28] and the solubility product of CaH_2SiO_4 presented by Greenberg and Chang [3] at 25°C. The Davies equation is used for ionic strength correction at a specific C/S ratio. Since pH values are not reported for most of the experimental data, PHREEQE is allowed to use pH adjustment. Concentrations of Ca_{total} and Si_{total} are taken from experimental data to obtain SI_i values for a specific C/S ratio; SI_i values are then converted to activities using Eq. (16). The activities determined from the experimental data of Kalousek [4] are used to calculate the empirical parameters by least square fitting with Eq. (5) because the Kalousek data are at 25°C. In the fitting procedure, recent studies [16–20] on the phase transition in the C-S-H gel are taken into account. In this work, we fix the point at C/S = 1.5 where the activity of $Ca(OH)_2(s)$ is unity. Values from the region at C/S > 1.5 where C-S-H gel coexist with $Ca(OH)_2(s)$ are omitted from the fitting procedure. The other data [3,5,6,8] are used to compare with model calculations. Since Si_{total} concentrations in the experimental data are very scattered in the region C/S > 1, it is quite difficult to evaluate the values of empirical parameters with the activities of $CaH_2SiO_4(s)$ by fitting with Eq. (6). However, the same values of α_0 and α_1 determined from Eq. (5) are used in Eq. (6) because the values should be the same in both Eqs. (5) and (6). The fitted values of the empirical parameters are shown in Table 1. The uncertainties of these empirical parameters listed in Table 1 are rather high because of data scatter. The uncertainties are determined at one standard deviation from the fitted curve.

Table 1
Fitted values of emperical parameters α_0 and α_1

Model solids	Fitted value
$Ca(OH)_2(s)$	$\alpha_0 = 1.235 \pm 0.137$
$CaH_2SiO_4(s)$	$\alpha_1 = 3.711 \pm 0.411$

Fig. 1 shows the calculated activities of $Ca(OH)_2(s)$ as a function of C/S ratio together with the activities measured experimentally [3–6,8], while Fig. 2 represents the calculated activities of $CaH_2SiO_4(s)$. The standard deviation σ in Fig. 1 between model calculation and experimental data of Kalousek [4] is 0.239 according to Eq. (17)

$$\sigma = \sqrt{\frac{\sum (y - y_i)^2}{N}} \tag{17}$$

where y and y_i are model and experimental results, respectively, and *N* is the number of data points.

Model calculations (shown by a solid line in Fig. 1) are comparable with the upper values of the experimental results. However, deviation between measured and modeled results is observed in this study. The reasons for the deviation may be as follows. First, these experiments are performed at 17–30°C. Second, Si_{total} concentrations are scattered in the experimental data, especially in the region C/S > 1 compared with Ca_{total}. These effects may be influenced by the saturation indices, which are used to calculate the activi-

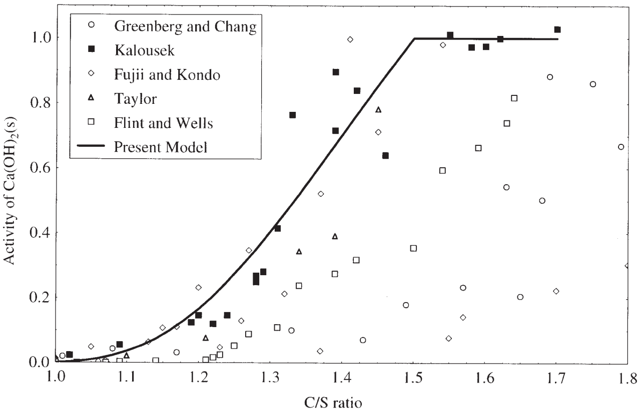

Fig. 1. Activities of $Ca(OH)_2(s)$ as a function of C/S ratio.

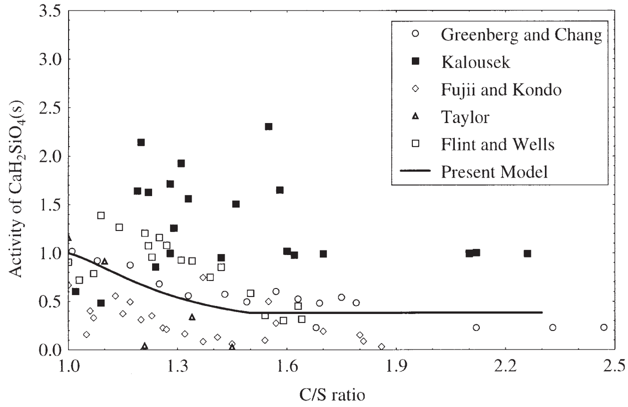

Fig. 2. Activities of $CaH_2SiO_4(s)$ as a function of C/S ratio.

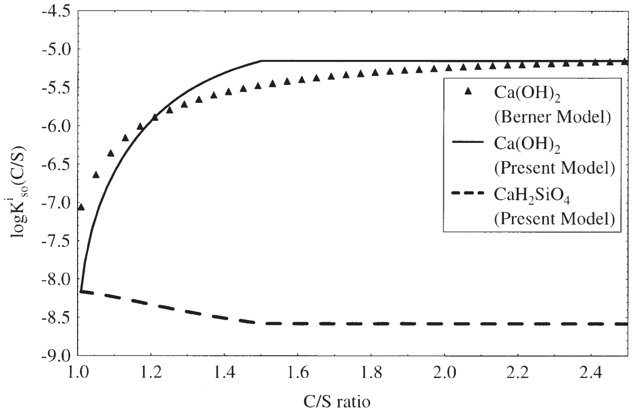

Fig. 3. Conditional solubility products of model solids and comparison with Berner [10] model at C/S > 1.

ties of the model solids. Third, different experimental and analytical procedures in the experiments [3–6,8] may have influenced the results in the C-S-H gel systems.

In Fig. 2, the calculated activities of $CaH_2SiO_4(s)$ are comparable with experimental values [3–6,8]. However, the deviation between measured and model results are large because of large scatter in Si_{total} at $C/S > 1$.

3.2. Solubility calculations

The mathematical expressions proposed in the model are used to calculate the solubility of C-S-H gel with charge and mass balances. Eqs. (12) and (13) are used for the conditional solubility products of $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$ at $1 < C/S \leqslant 1.5$ in the solubility calculations. The values of $\log K^1_{SO}(C/S)$ and $\log K^2_{SO}(C/S)$ are found to be -5.15 and -8.58 using Eqs. (12) and (13), respectively, at $C/S = 1.5$. These values are used over $C/S > 1.5$ in the solubility calculations. A set of dissolved species such as Ca^{2+}, $CaOH^+$, $H_2SiO_4^{2-}$, $H_3SiO_4^-$, H_4SiO_4, H^+, and OH^- is assumed to present in the system at equilibrium [10]. The chemical reactions of these species are also used to calculate the solubility in the system. The charge balance of the system is expressed by these species. The ionic strength is corrected by applying the Davies equation [29]. The aqueous concentrations of species, Ca^{2+} and $CaOH^+$, are used to calculate Ca_{total} in solution. Si_{total} concentrations are calculated from the aqueous concentrations of $H_2SiO_4^{2-}$, $H_3SiO_4^-$, and H_4SiO_4. The chemical reactions used for the solubility calculations are listed in Table 2. The databases MINEQL [26] and PHREEQE [27] are used for solubility calculation as shown in Table 2.

The values of $\log K^1_{SO}(C/S)$ and $\log K^2_{SO}(C/S)$ together with the conditional solubility product of $Ca(OH)_2(s)$ in the Berner model are shown in Fig. 3. The values of $\log K^1_{SO}(C/S)$ obtained in this work are found to be lower and higher than those of the Berner model at $C/S < 1.2$ and at $C/S > 1.2$, respectively. At $C/S = 1.5$, the values of $\log K^1_{SO}(C/S)$ is -5.15, while the same value of conditional solubility product is found at $C/S = 2.5$ in the Berner model. This is because the integration constant derived from Gibbs-Duhem equation is variable with respect to C/S ratio in this work, while a constant value is taken in the Berner model. On the other hand, the value of $\log K^2_{SO}(C/S)$ is taken as a constant value (-8.16) in the Berner model, while variable values of $\log K^2_{SO}(C/S)$ with C/S ratio are taken in our present work as $1 < C/S \leqslant 1.5$. In addition, the conditional solubility products of model solids in the Berner model are used as a fitting parameter to describe the solubility behavior of the C-S-H gel. In the present model, we use the activities of model solids to extract the conditional solubility

Table 2
Chemical reactions and their equilibrium constants log *K* used for solubility calculations

Chemical reactions	log *K*	References
$Ca^{2+} + OH^- \leftrightarrow CAOH^+$	−1.22	[26]
$H_2SiO_4^{2-} + H_2O \leftrightarrow H_3SiO_4^- + OH^-$	0.67	[26]
$H_2SiO_4^{2-} + 2H_2O \leftrightarrow H_4SiO_4 + 2OH^-$	4.86	[26]
$H_2O \leftrightarrow H^+ + OH^-$	14.0	[26]
$Ca(OH)_2(s) \leftrightarrow Ca^{2+} + 2OH^-$	−5.15	[26, 27]
$CaH_2SiO_4(s) \leftrightarrow Ca^{2+} + H_2SiO_4^{2-}$	−8.16	[26]

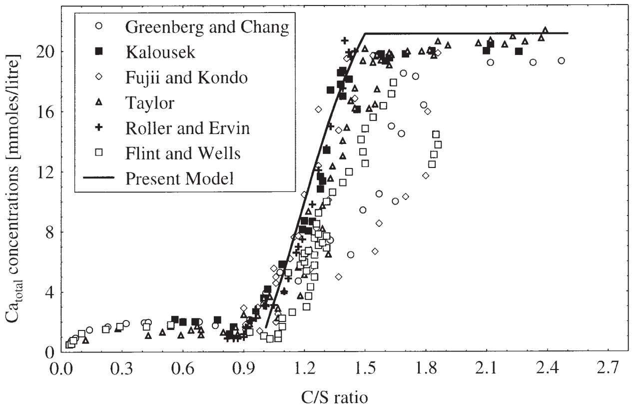

Fig. 4. Measured [3–8] and modeled Ca_{total} concentrations in solution of the C-S-H gel system.

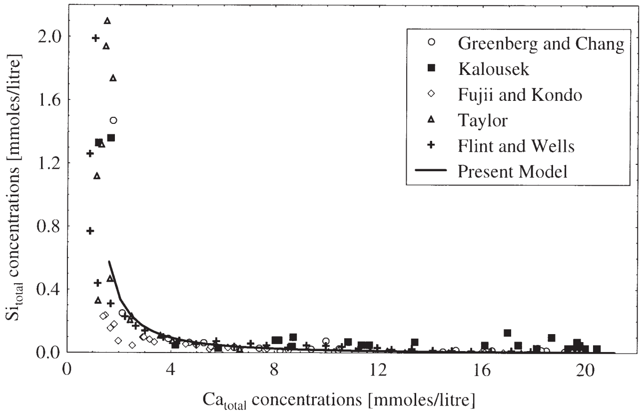

Fig. 5. Measured [3–6,8] and modeled Si$_{total}$ concentrations in solution of the C-S-H gel System.

products of $Ca(OH)_2(s)$ and $CaH_2SiO_4(s)$ by considering recent studies [16–20] on the phase transition of C-S-H gel.

The Ca$_{total}$ concentrations in solution calculated by the proposed model relatively agree with experimental data [3–8] of C-S-H gel system as shown in Fig. 4. The Si$_{total}$ concentrations in solution as shown in Fig. 5 are also comparable with experimental data [3–6,8]. The pH values in the model calculations are found between 11.4 to 12.48, which are comparable with those of Greenberg and Chang [3], shown in Fig. 6.

Due to lack of corresponding thermodynamic data, the model is restricted to 25°C. Since the solubility calculations are based on the thermodynamic data, model calculations could be further improved by redetermining the input data.

The present model is limited to the C-S-H gel system. However, the interactions of cementitious material with water develop other hydrated phases. In the real system, these phases may interact with or substitute in C-S-H gel. The substitution of Si or Ca from the dissolution of C-S-H gel to other phases may have significant effect on the concentrations of Si$_{total}$ and Ca$_{total}$ in the real system. Stade and Muller [30] suggested that C-S-H gel of high C/S ratio contained layers of portlandite structure, in which Ca can be replaced by Al or Fe to form a layer of monosulfate structure. Furthermore, based on the evidence including X-ray data it is reported that Al^{3+} enters C-S-H gel by joining with H^+ to replace Si^{4+} or by joining with another Al^{3+} to replace $3Ca^{2+}$ [31]. Si^{4+} replacement for SO_4^{2-} may be due to the existence of ettringite in the hydrated cement phases [32].

In our present study, the effects of these replaceable ions on the dissolution of C-S-H gel are not considered. In the near future, a model for the effects of ettringite, monosulfate, hydrogarnet, and gypsum on the dissolution of C-S-H gel will be developed.

4. Conclusions

A model for dissolution of C-S-H gel is developed by assuming a nonideal mixture of Margules-type solid solutions. The proposed model can reproduce the solubility data of C-S-H gel system. The calculated results of Ca$_{total}$ and Si$_{total}$ concentrations and pH values by this model are comparable with experimental results. This model is a useful tool to predict the safety assessment of radioactive waste disposal.

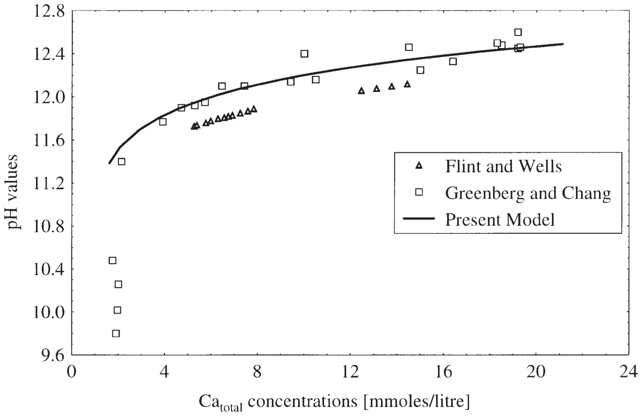

Fig. 6. Measured [3,8] and modeled pH values in the C-S-H gel System.

References

[1] F.B. Neall, Modelling of the near-field chemistry of the SMA repository at the Wellenberg site, Paul Scherrer Institute, Switzerland, PSI Bericht Nr., 94-18, 1994.

[2] E.J. Reardon, Problems and approaches to the prediction of the chemical composition in cement/water systems, Waste Management 12 (1992) 221–239.

[3] S.A. Greenberg, T.N. Chang, Investigation of the colloidal hydrated calcium silicates. II. Solubility relationships in the calcium oxide-silicate-water system at 25°, J Phys Chem 69 (1965) 182–188.

[4] G.L. Kalousek, Application of different thermal analysis in a study of the system lime-silica-water, Proc. 3rd Int. Symp. on Chem. of Cements, London, 1952, p. 296.

[5] K. Fujii, W. Kondo, Heterogeneous equilibrium of calcium silicate hydrate in water at 30°C, J Ceram Soc Dalton Trans 2 (1981) 645–651.

[6] H.F.W. Taylor, Hydrated calcium silicates. Part I. Compound formation at ordinary temperatures, J Chem Soc London 276 (1950) 3682–3690.

[7] P.S. Roller, G. Ervin Jr., The system calcium oxide-silicate-water at 30°C. The association of silicate ion in dilute alkaline solution, J Am Chem Soc 62 (1940) 461–471.

[8] E.P. Flint, L.S. Wells, Study of the system $CaO-SiO_2-H_2O$ at 30°C and of the reaction of water on the anhydrous calcium silicates, J Res NBS 12 (1934) 751–783.

[9] H.M. Jennings, Aqueous solubility relationships for two types of calcium silicates hydrate, J Am Ceram Soc 69 (1986) 614–618.

[10] U. Berner, A thermodynamic description of the evolution of pore water chemistry and uranium speciation during the degradation of cement, Paul Scherrer Institute, Switzerland, PSI-Bericht Nr. 62, 1990.

[11] A. Atkinson, J.A. Hearne, C.F. Knights, Aqueous chemistry and thermodynamic modelling of $CaO-SiO_2-H_2O$ gels, DOE Report RW/87.048, AERE-R12548, 1987.

[12] S. Borjesson, A. Emren, C. Ekberg, A thermodynamic model for the calcium silicate hydrate gel, modelled as a non-ideal binary solid solution, Cem Concr Res 27 (1997) 1649–1657.

[13] F.P. Glasser, D.E. Macphee, E.E. Lachowski, Solubility modelling of cements: Implications for radioactive waste immobilization, Mat Res Soc Symp Proc 84 (1987) 331–341.

[14] S.A. Greenberg, T.N. Cheng, E. Anderson, Investigation of colloidal hydrated calcium silicates. I. Solubility products, J Phys Chem 64 (1960) 1151–1157.

[15] D.L. Kantro, S. Brunauer, C.H. Weise, Development of surface in the hydration of calcium silicates. II. Extension of investigations to earlier and later stages of hydration, J Phys Chem 66 (1962) 1804–1809.

[16] H.F.W Taylor, Cement Chemistry, 1st ed., Academic Press, London, 1990.

[17] H. Stade, W. Wieker, Structure of ILL-crystallized calcium hydrate silicates: I. Formation and properties of an ILL-crystallized calcium hydrate silicate phase, Z Anorg Allg Cem 466 (1980) 55–70.

[18] M. Grutzeck, A. Benesi, B. Fanning, Silicon-29 magic angle spinning nuclear magnetic resonance study of calcium silicate hydrates, J Am Ceram Soc 72 (1989) 665–668.

[19] A. Nonat, X. Lecoq, The structure, stoichiometry and properties of C-S-H prepared by C_3S hydration under controlled condition, Proc. Int. Conf. on NMR Spectroscopy of Cement Based Material, Bergame, 1996, pp. 197–207.

[20] I. Klur, B. Pollet, J. Virlet, A. Nonat, C-S-H structure evolution with calcium content by multinuclear NMR, Proc. Int. Conf. on NMR Spectroscopy of Cement Based Material, Bergame, 1996, pp. 119–141.

[21] J.M. Prausnitz, Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice-Hall, Inc., Engelwood Cliffs, New Jersey, 1969, p. 523.

[22] M. Margules, Uber die zussamensetzung der gesattignten dampfe von mischungen, Sitzungsber Wien Akad 104 (1985) 1243–1278.

[23] S.K Saxena, Thermodynamics of rock-forming solution, Springer-Verlag, Berlin, 1973, p. 188.

[24] P.D. Glynn, MBSSAS: A code for the computation of Margules parameters and equilibrium relations in binary solid-solution aqueous-solution systems, Comput Geoscie 17 (1991) 907–966.

[25] M. Kersten, Aqueous solubility diagrams for cementitious waste stabilization systems. 1. The C-S-H solid-solution system, J Environ Sci Technol 30 (1996) 2286–2293.

[26] J.C. Westall, J.L. Zachary, F.M. Morel, MINEQL—A computer program for the calculation of chemical equilibrium composition of aqueous systems, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1976.

[27] D.L. Parkhurst, D.C. Thorstenson, L.N. Plummer, PHREEQE—A computer program for geochemical calculations, U.S. Geological Survey, Water-Resources Investigations, 80-96, 1980.

[28] CHEMVAL6, Thermodynamic Database Version 6, HMIP P3/008A, London, 1995.

[29] W. Stumm, J.J. Morgan, Aquatic Chemistry, 3d ed., John Wiley & Sons, Inc., New York, 1996, p. 103.

[30] H. Stade, D. Muller, On the coordination of Al in ILL-crystallized C-S-H phases formed by hydration of tricalcium silicate and by precipitation reactions at ambient temperature, Cem Concr Res 17 (1987) 553–561.

[31] M.L.D. Gougar, B.E. Scheetz, D.M. Roy, Ettringite and C-S-H portland cement phases for waste ion immobilization: A review, Waste Management 16 (1996) 295–303.

[32] M. Atkins, F.P. Glasser, A. Kindness, Phase relations and solubility modelling in the CaO-SiO_2-Al_2O_3-MgO-SO_3-H_2O system: For application to blended cement, Mat Res Soc Symp Proc 212 (1991) 387–394.