Cement and Concrete Research 38 (2008) 1270–1275

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Chemical alteration of calcium silicate hydrate (C–S–H) in sodium chloride solution

Daisuke Sugiyama *

Nuclear Technology Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), 2-11-1, Iwado-kita, Komae-shi, Tokyo 201-8511, Japan

ARTICLE INFO

Article history:
Received 15 February 2007
Accepted 6 June 2008

Keywords:
Calcium silicate hydrate (C–S–H)
Dissolution
Cation exchange
Sodium
Thermodynamic modelling

ABSTRACT

The effect of sodium chloride on the chemical alteration of calcium silicate hydrate (C–S–H) was measured and discussed. The release of calcium from C–S–H was increased as the concentration of sodium chloride in the solution increased. It was observed that sodium sorbed onto the C–S–H phases and some sodium replaced calcium in C–S–H so that the release of calcium was enhanced. An integrated modelling approach employing an ion-exchange model and an incongruent dissolution model of C–S–H is developed. It reasonably and accurately predicted the release of calcium from C–S–H in sodium chloride solution by considering cation exchange and the effect of the ionic strength on the solubility of C–S–H.

1. Introduction

For radioactive waste disposal in Japan, cement is a potential waste packaging and backfilling material and is expected to provide effective chemical containment [1]. In particular, the ability to provide high-pH condition is a very important factor when considering the release of radionuclides from radioactive waste, since the solubility is low and the sorption distribution ratio is high for many radioactive species at high pHs. High pH condition depends on the solubility of constituent hydrated minerals in cement matrices. For the long-term safety assessment of radioactive waste disposal, it is necessary to develop a series of predictive calculation models for the behaviour of the repository system. Several models have been proposed for the incongruent dissolution of calcium silicate hydrate (C–S–H) gel, which is the principal product of hydrated cement phases and mainly determines the pH condition in the near field [2–6]. All these models reproduce the available solubility data for C–S–H gel in water [7–10] reasonably well.

In the presence of some reactive ions in groundwater, the chemical alteration of cement materials is affected. Duerden et al. [11] measured the dissolution of C–S–H and $Ca(OH)_2$ in sodium chloride solution ($NaCl \leq 1.5$ mol dm^{-3}) and observed that calcium solubility increases in this solution compared with that in distilled water. However, the mechanism of the effect of NaCl on the dissolution of C–S–H is not yet fully understood.

In this study, the dissolution of C–S–H (with Ca/Si = 0.65 0.83, 0.9, 1.1 and 1.2) in sodium chloride solution is measured, in which the sorption of sodium onto C–S–H is observed. To discuss the mechanism of the release of calcium from C–S–H, experiments on the sorption of caesium and strontium onto C–S–H in sodium chloride solution are also carried out. On the basis of the experimental results, a modelling approach employing the ion-exchange model and the incongruent dissolution model of C–S–H is developed.

2. Experimental

C–S–H samples with Ca/Si ratios of 0.65, 0.83, 0.9, 1.1 and 1.2 were prepared by mixing appropriate amounts of CaO with amorphous silica in distilled water and aging the mixture for at least 7 days. This synthesis procedure is similar to that employed by Atkins et al. [12]. The hydrated samples were dried at room temperature in a vacuum desiccator above silica gel, then powdered and passed through a 250 µm sieve. The prepared solids were each determined as single-phase solid C–S–H by X-ray diffraction analysis since no phases other than C–S–H were identified, as shown in Fig. 1. The concentrations of calcium and silica in each supernate were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the chemical composition of the prepared C–S–H solid was determined by considering the material balance. C–S–H samples with Ca/Si ratios of 0.65, 0.83, 0.90, 1.1 and 1.2 were obtained.

C–S–H dissolution experiments in sodium chloride solution were carried out at a liquid:solid ratio of 100:1 [cm^3 g^{-1}] using a method similar to the batch sorption technique. All experiments were carried out in duplicate at room temperature in an Ar-filled ($O_2 < 2$ ppm) glovebox.

Powdered C–S–H gel samples (Ca/Si = 0.65, 0.83, 0.9, 1.1 and 1.2) were equilibrated with distilled water for at least 30 days at the same liquid:solid ratio as that used in the sorption experiments (100:1) in 50 cm^3 polypropylene centrifuge tubes. After the preequilibration, the tubes were centrifuged and the supernates were removed. The pHs of the preequilibrated solutions measured using a glass electrode were

---

* Tel.: +81 3 3480 2111; fax: +81 3 3480 3564.
E-mail address: daisukes@criepi.denken.or.jp.

0008-8846/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2008.06.002

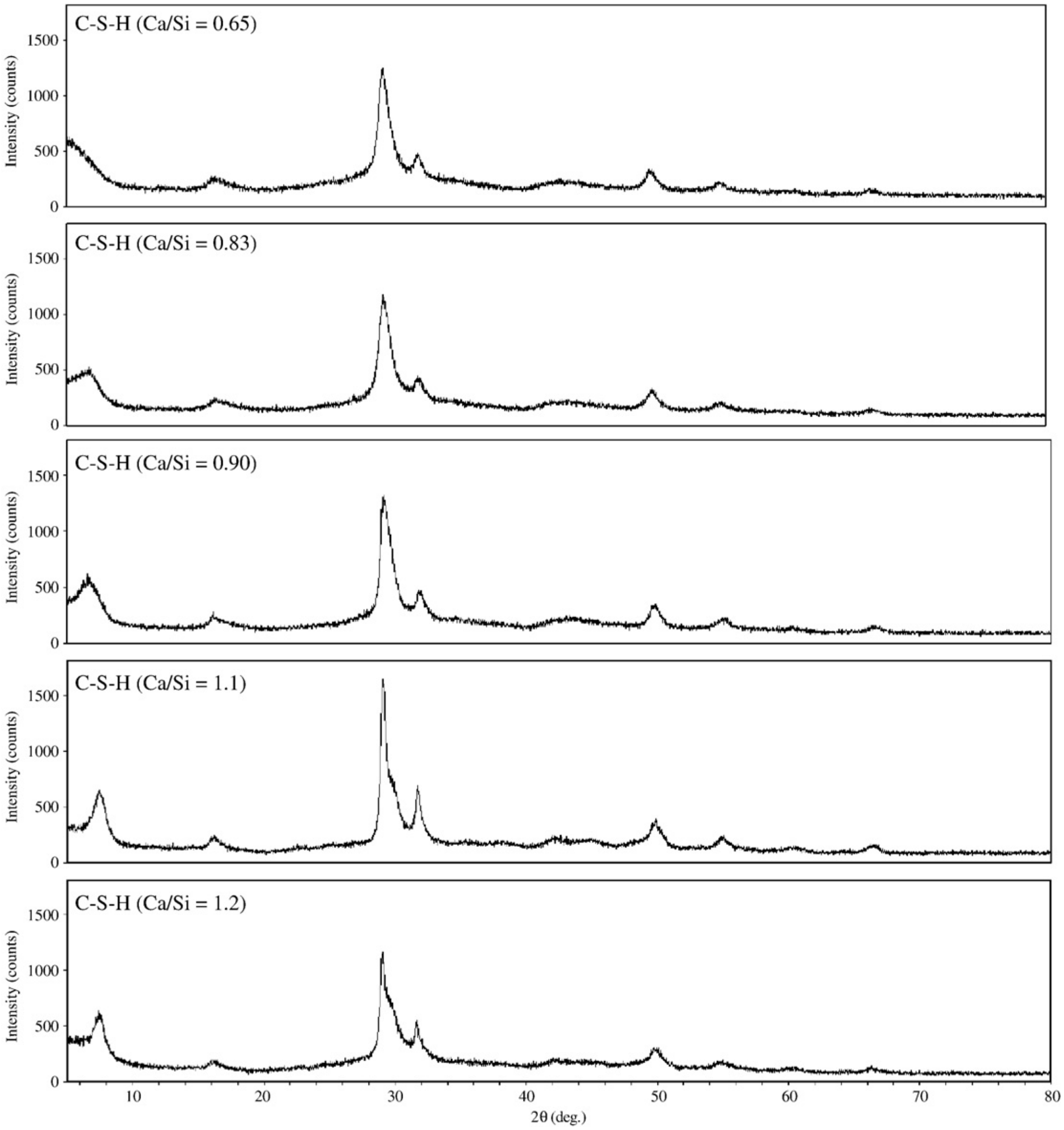

Fig. 1. X-ray diffraction patterns of prepared C–S–H solids.

10.2, 11.0, 11.3, 11.8 and 11.9 for C–S–H with initial Ca/Si ratios of 0.65, 0.83, 0.90, 1.1 and 1.2, respectively. Each solution was filtered through a 30,000 MWCO filter and analysed for calcium and silica by ICP-AES, so that the Ca/Si ratios of the preequilibrated C–S–H samples could be calculated. The Ca/Si ratios of the preequilibrated solids were 0.66, 0.83, 0.88, 1.03 and 1.08 for initial Ca/Si ratios of 0.65, 0.83, 0.90, 1.1 and 1.2, respectively. Each centrifuge tube containing C–S–H was weighed to determine the volume of equilibrated solution removed. Sodium chloride was added to each 30,000-MWCO-filtered preequilibrated solution to give initial concentrations of 1.0×10^{-4}, 1.0×10^{-3}, 3.6×10^{-3}, 1.0×10^{-2}, 1.0×10^{-1} and 6.2×10^{-1} mol dm^{-3}; as extra precaution, the solutions were passed through a 0.45 µm membrane filter after the addition of sodium chloride. The initial sodium concentration was measured by atomic absorption spectrometry. The required volume of solution (equal to the volume of equilibrated solution removed determined above) was returned to the appropriate centrifuge tube containing C–S–H, and sorption was started at this point. Contact between sodium chloride solution and C–S–H was maintained for at least 45 days. After equilibration, pH was measured and no significant change (>0.2) was observed.

Experiments on the sorption of caesium and strontium onto C–S–H with Ca/Si = 0.9 were carried out at a liquid:solid ratio of 100:1 [cm^3 g^{-1}] using the batch sorption technique, which was similar to that used in the sodium experiment. The initial concentrations of caesium chloride and strontium chloride were 5.0×10^{-5}, 5.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3} and 2.0×10^{-2} mol dm^{-3}. The caesium and strontium chloride solutions were prepared by equilibrating 1×10^{-4} mol dm^{-3} sodium chloride solution with C–S–H (Ca/Si = 0.9).

The chemical composition of each equilibrated solution was analysed after passing the sorption through a 0.45 µm membrane filter. The equilibrated concentrations of sodium and caesium were measured by atomic absorption spectrometry. The equilibrated concentrations of calcium, silica and strontium were measured by ICP-AES. Each filtered solution was acidified and diluted with known volumes of 1 mol dm^{-3} HNO_3 solution and distilled water before analysis to make the concentrations of the target and matrix elements appropriate for the analysis.

3. Results

The agreement between the duplicate results was within or close to the uncertainty of the analysis (5%) for all cases. In the experiments on C–S–H dissolution in sodium chloride solution, the measured calcium concentration increased as sodium chloride concentration increased, as shown in Fig. 2. (Note that the Ca/Si ratios shown in Figs. 2–8 are the initial values before the preequilibration.) The effect

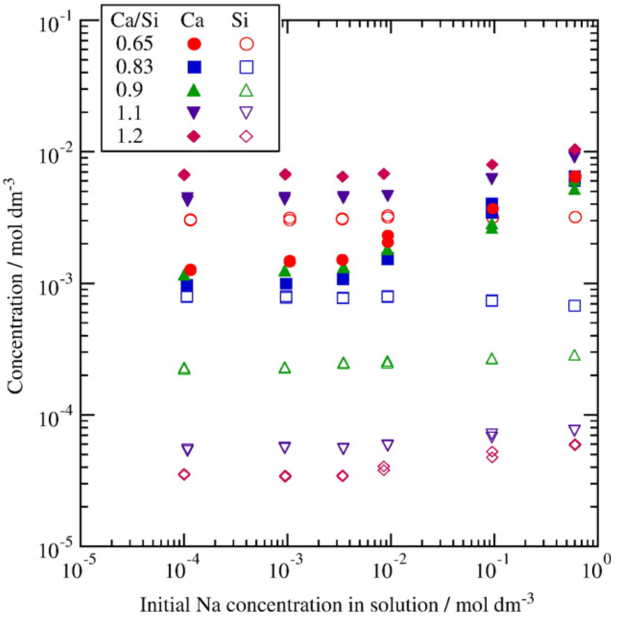

Fig. 2. Measured calcium and silica concentrations for various sodium chloride concentrations.

of sodium chloride concentration on the enhancement of calcium release from C–S–H was stronger at lower Ca/Si ratios.

In the caesium and strontium sorption experiments on C–S–H in sodium chloride solution, the measured calcium concentration increased as caesium or strontium concentration increased. The material balance calculated using the initial and equilibrated concentrations of calcium, caesium and strontium is shown in Fig. 3. A linear relationship between the amount of calcium leached from C–S–H gel (Ca/Si = 0.9) and the amount of sorbed caesium or strontium was observed. The slopes for sorption were 0.5 for caesium and 1.0 for strontium, which suggest that 2 mol of caesium and 1 mol of strontium sorb onto C–S–H gel by replacing 1 mol of calcium in C–S–H gel.

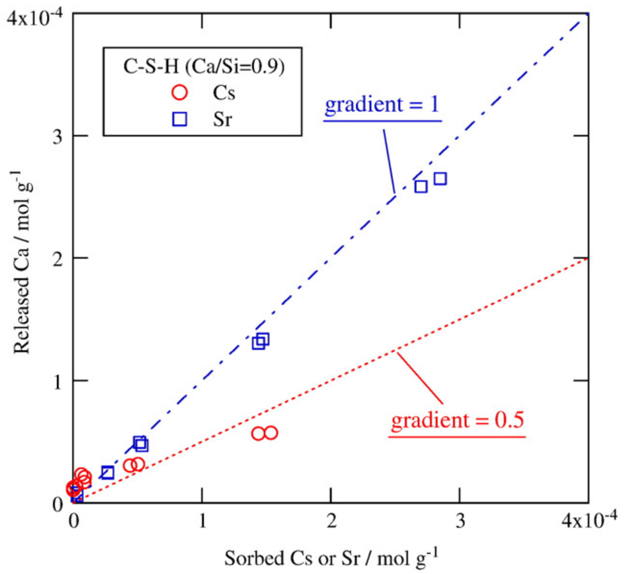

Fig. 3. Dependence of amount of calcium leached from C–S–H gel on sorbed caesium and strontium concentrations.

The material balance was calculated using the initial and equilibrated calcium and sodium concentrations and is shown in Fig. 4. For sodium, no clear relationship of the exchange of sodium and calcium was observed compared with the cases of caesium and strontium. However, it appeared that there is a linear relationship between the amount of calcium released from C–S–H and the amount of sorbed sodium on C–S–H at sorbed sodium concentrations $< 5\times10^{-4}$ mol g^{-1}, although a certain amount of scatter of the data points was observed. The slope for the sorption was approximately 0.5, which suggested that 2 mol of sodium sorbed onto C–S–H by replacing 1 mol of calcium in C–S–H. At sorbed sodium concentrations $> 5\times10^{-4}$ mol g^{-1}, the data departed from the linear trend, but the result still suggests that some sodium replaced calcium in C–S–H.

One possible interpretation of the difference between the results for caesium and sodium is that the Stokes radius of caesium is smaller than that of sodium so that caesium could be more easily incorporated into the C–S–H structure by substitution than sodium. If this were the case, sodium would have been sorbed onto C–S–H by other mechanisms, e.g., surface complexation, at higher sodium concentrations. More experimental data are needed to discuss the mechanism of sodium sorption onto C–S–H in more detail.

4. Discussion

4.1. Model development

Based on the experimental data, an approach in which the ion-exchange mechanism is assumed to predominate the sorption of caesium, strontium and sodium onto C–S–H gel can be employed. Also, the aqueous calcium concentration should be influenced not only by cation exchange reactions but also by the incongruent dissolution of C–S–H. In this study, therefore, an integrated approach that uses the cation-exchange model to describe the sorption of sodium onto C–S–H and the incongruent dissolution model of C–S–H is developed and discussed to interpret the experimental data.

It is important to predict the likely speciation of each element under experimental conditions since the speciation is a determining factor that must be considered when interpreting exchange reactions. Therefore, speciation calculation was carried out using the geochemical code PHREEQC [13] and the thermodynamic database HATCHES [14] version NEA15. The predominant species of sodium, caesium, strontium and calcium at $10 < pH < 12$ were predicted to be Na^+(100%), Cs^+(100%) , Sr^{2+}(>95%) and Ca^{2+}(>84%), respectively.

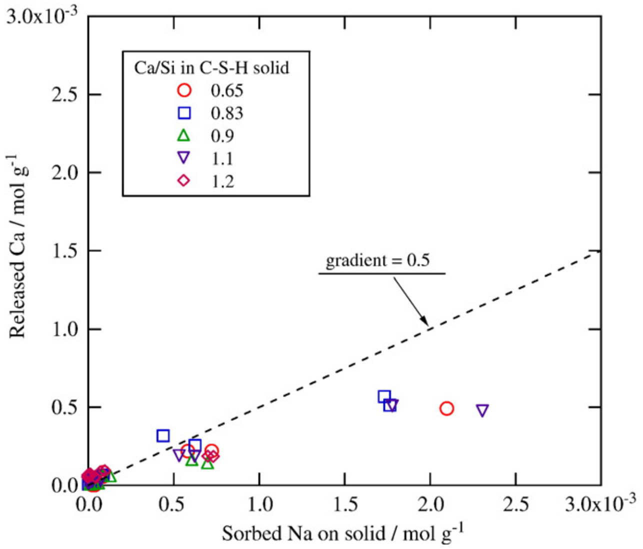

Fig. 4. Dependence of amount of calcium leached from C–S–H gel on sorbed sodium concentration.

On the basis of the above discussion, the cation exchanges of sodium, caesium and strontium with calcium in C–S–H can be represented as the reversible reactions

$$\overline{\mathrm{Ca}} + 2\mathrm{Na}^{+} = 2\overline{\mathrm{Na}} + \mathrm{Ca}^{2+}, \tag{1}$$

$$\overline{\mathrm{Ca}} + 2\mathrm{Cs}^{+} = 2\overline{\mathrm{Cs}} + \mathrm{Ca}^{2+}, \tag{2}$$

$$\overline{\mathrm{Ca}} + \mathrm{Sr}^{2+} = \overline{\mathrm{Sr}} + \mathrm{Ca}^{2+}, \tag{3}$$

where $\overline{\mathrm{Ca}}$, $\overline{\mathrm{Na}}$, $\overline{\mathrm{Cs}}$ and $\overline{\mathrm{Sr}}$ are the exchanging ions in the C–S–H solid.

The thermodynamic equilibrium constant (K) for the reaction can be defined by

$$K_{\mathrm{Na}} = \frac{\overline{X_{\mathrm{Na}}}^{2} \cdot \left(\gamma_{\mathrm{Ca}^{2+}} \cdot \left[\mathrm{Ca}^{2+}\right]\right)}{\overline{X_{\mathrm{Ca}}} \cdot \left(\gamma_{\mathrm{Na}^{+}} \cdot \left[\mathrm{Na}^{+}\right]\right)^{2}}, \tag{4}$$

$$K_{\mathrm{Cs}} = \frac{\overline{X_{\mathrm{Cs}}}^{2} \cdot \left(\gamma_{\mathrm{Ca}^{2+}} \cdot \left[\mathrm{Ca}^{2+}\right]\right)}{\overline{X_{\mathrm{Ca}}} \cdot \left(\gamma_{\mathrm{Cs}^{+}} \cdot \left[\mathrm{Cs}^{+}\right]\right)^{2}}, \tag{5}$$

$$K_{\mathrm{Sr}} = \frac{\overline{X_{\mathrm{Sr}}} \cdot \left(\gamma_{\mathrm{Ca}^{2+}} \cdot \left[\mathrm{Ca}^{2+}\right]\right)}{\overline{X_{\mathrm{Ca}}} \cdot \left(\gamma_{\mathrm{Sr}^{2+}} \cdot \left[\mathrm{Sr}^{2+}\right]\right)}, \tag{6}$$

where $\overline{X_{\mathrm{Ca}}}$, $\overline{X_{\mathrm{Na}}}$, $\overline{X_{\mathrm{Cs}}}$ and $\overline{X_{\mathrm{Sr}}}$ are the equivalent fractions of exchanging ions in the C–S–H solid, γ_i are the activity coefficients of exchanging ions in the solution, and the brackets denote the concentrations of exchanging ions in mol dm^{-3}. The initial amount of total exchangeable calcium is assumed to be the total concentration of calcium in the C–S–H at the start of sorption, in mol dm^{-3}. The concentration of each exchange species is calculated using aqueous concentration data by considering the material balance. The Davies equation was used for ionic strength correction to calculate the activity coefficients.

The calculated log K values for the cation exchange reactions for Eqs. (1)–(3) are shown in Fig. 5 (a) and (b). Although there is a spread of the data points shown in Fig. 5 (a) and (b), the log K values are estimated as follows: log $K_{\mathrm{Na}}=-2.9$ (±0.5) for sodium, log $K_{\mathrm{Cs}}=-3.2$ (±0.4) for caesium, and log $K_{\mathrm{Sr}}=-1.5$ (±0.3) for strontium. One reason for the scatter of the data points may be the uncertainty in the solubility of amorphous C–S–H [2,6] and in the solubility of Na-, Cs- or Sr-substituted C–S–H. For strontium sorption, there might have been a saturation of exchanging sites with strontium at higher strontium concentrations.

The thermodynamic incongruent dissolution model of C–S–H proposed by Sugiyama and Fujita [6] is employed in the modelling approach. In the incongruent C–S–H dissolution model, in which C–S–H is assumed to be a binary non-ideal solid solution of $\mathrm{Ca(OH)_2}$ and $\mathrm{SiO_2}$, the log K values of the model end members of the solid solution are given as functions of the Ca/Si ratio of C–S–H [6]:

$$\log K_{\mathrm{s}} = \frac{1}{1+y} \cdot \log K_{\mathrm{s0}} - \frac{1}{1+y} \cdot \log \frac{1}{1+y} + \frac{y}{(1+y)^{2}} \cdot \left[A'_{\mathrm{s0}} + A'_{\mathrm{s1}}\left(\frac{1-y}{1+y}\right) + A'_{\mathrm{s2}}\left(\frac{1-y}{1+y}\right)^{2}\right], \tag{7}$$

$$\log K_{\mathrm{c}} = \frac{y}{1+y} \cdot \log K_{\mathrm{c0}} - \frac{y}{1+y} \cdot \log \frac{y}{1+y} + \frac{y}{(1+y)^{2}} \cdot \left[A'_{\mathrm{c0}} + A'_{\mathrm{c1}}\left(\frac{1-y}{1+y}\right) + A'_{\mathrm{c2}}\left(\frac{1-y}{1+y}\right)^{2}\right], \tag{8}$$

y=Ca/Si of C–S–H, $\log K_{\mathrm{s0}}=-2.710$, $\log K_{\mathrm{c0}}=22.81$ [14].
At Ca/Si ≤ 0.461, $\log K_{\mathrm{s}}=\log K_{\mathrm{s0}}-\log(1+y)$.
At 1.755 ≤ Ca/Si, $\log K_{\mathrm{s}}=-7.853$, $\log K_{\mathrm{c}}=22.81$.

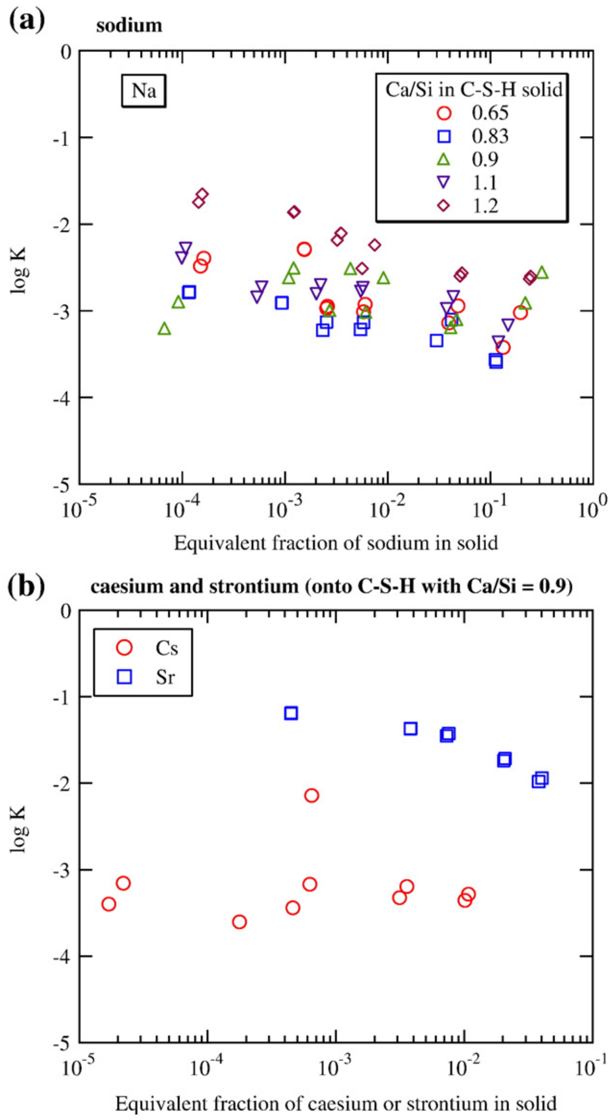

Fig. 5. Estimated log K values for cation exchange reactions of sodium, caesium and strontium with calcium in C–S–H. (a) sodium. (b) caesium and strontium (onto C–S–H with Ca/Si = 0.9).

The fitted empirical parameters (A_{ij}) are shown in Table 1. This model was adopted in the study because the simplicity of its numerical description allows its inclusion in the chemical equilibrium calculations with the common approach of using the law of mass action (log K) in PHREEQC.

4.2. Modelling results

All modelling calculations were carried out using PHREEQC [13], which has the capability of calculating ion-exchange equilibria, and the thermodynamic database HATCHES [14] version NEA15.

The results obtained using the integrated model for the dependence of the release of the calcium from C–S–H on sodium chloride concentration are shown in Fig. 6, along with the sodium sorption experimental results for comparison. The measured concentrations of calcium and silica were reasonably accurately predicted by considering the cation-exchange reaction together with the incongruent dissolution of C–S–H, as shown in Fig. 6. In Fig. 7, the results obtained using developed approach are compared with the results obtained using only the incongruent C–S–H dissolution model. At elevated sodium chloride concentrations, the solubility of C–S–H is predicted to

Table 1
Fitted values of empirical parameters at 25 °C [6]

End member	SiO_2			$Ca(OH)_2$		
A_{ij}	A'_{s0}	A'_{s1}	A'_{s2}	A'_{c0}	A'_{c1}	A'_{c2}
Ca/Si ≤ 0.833	−18.623	57.754	−58.241	37.019	−36.724	164.17
Ca/Si > 0.833	−18.656	49.712	25.033	36.937	−7.8302	−50.792

increase due to the decrease in the activity coefficients at higher ionic strengths. The sole use of the incongruent C–S–H dissolution model predicted the tendency of the increase in the solubility of calcium qualitatively, but there was still a substantial difference between the experimental and modelling data. As shown in Fig. 7, it is clearly demonstrated that the agreement between the experimental and modelling data could have been improved by integrating the cation-exchange model with the incongruent C–S–H dissolution model. The effect of sodium replacing the calcium of C–S–H upon the release of calcium is more noticeable at lower Ca/Si ratios of C–S–H; this was modelled reasonably and accurately using the integrated model. However, there is still a disagreement between the measured and calculated values. The reason for the difference is still unclear, but some possibilities can be suggested. Firstly, the effect of ionic strength on the solubility of C–S–H may not yet be fully understood, particularly at high sodium chloride concentrations. Secondly, the solubility of C–S–H may be affected when sodium replaces calcium in C–S–H. Although the structure of C–S–H gel is not yet fully understood, it has been shown that it has a nanostructure and is structurally similar to tobermorite [15]. Faucon et al. [16] defined two types of calcium in C–S–H: Ca in the octahedral layer and Ca in the interlayer of C–S–H sheets. Once some calcium in C–S–H has been replaced by sodium, the layer structure of C–S–H should be affected or disordered. Thus, the solubility of calcium from C–S–H will change. Thirdly, the results suggest that mechanisms (e.g., surface complexation) other than cation exchange should be considered to discuss the sorption of sodium onto C–S–H and the release of calcium from C–S–H.

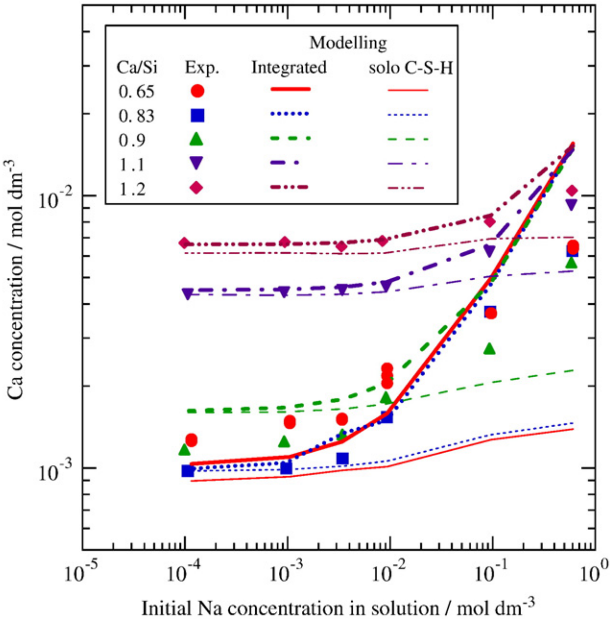

Fig. 7. Comparison of the developed model with the simple C–S–H dissolution calculation (calcium solubility).

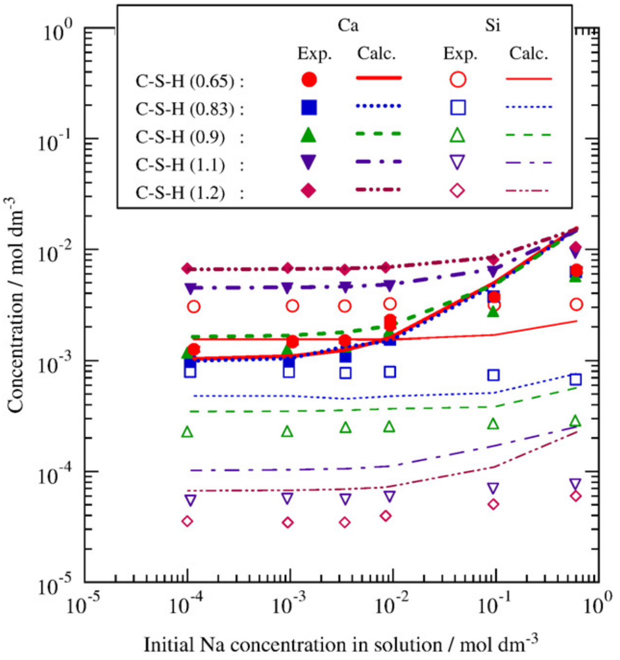

Fig. 6. Dependences of calcium and silica concentrations on sodium chloride concentration in sodium sorption experiment (experimental and modelling data).

Hong and Glasser [17] measured the sorption distribution ratio of sodium onto C–S–H (Ca/Si = 0.85, 1.2, 1.5 and 1.8) in NaOH solution. In their experiment, the calcium concentration in solution decreased as the sodium concentration increased over a range of 1–300 mmol dm^{-3}, as shown in Fig. 8. Modelling calculations were performed using the present (integrated) model and the results are shown in Fig. 8. The experimental data [17] have been reasonably well predicted using the present model. Note that Hong and Glasser used NaOH solution in their experiments [17], while we used NaCl solution in the present study. Consequently, the dissolution of calcium ($Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$) in NaOH solution is restricted at higher OH^- concentrations given by the NaOH concentration. The incongruent dissolution model employed in the present integrated model can take into account the restriction of calcium solubility in NaOH solution [6] so that the present model can successfully predict the data obtained by Hong and Glasser [17].

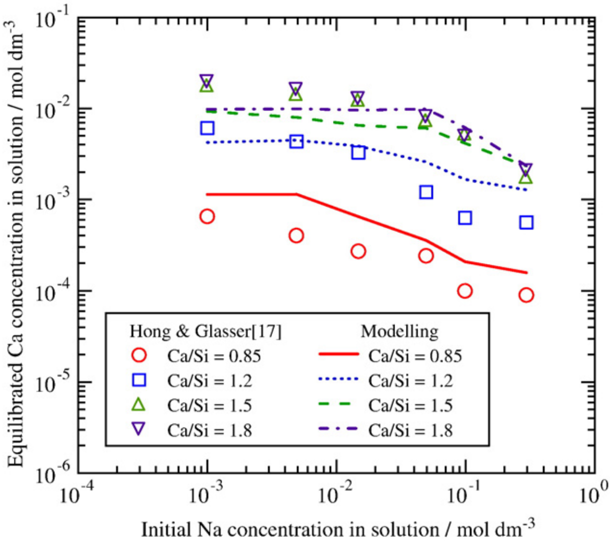

Fig. 8. Steady-state calcium concentration in solution as function of initial NaOH concentration (experimental data [17] and data calculated using the present model).

5. Conclusions

It was observed that sodium sorbed onto C–S–H and some sodium replaced calcium in C–S–H. The equilibrium constant for the exchange reaction of sodium with calcium in C–S–H was estimated, and an integrated modelling approach employing a cation-exchange model and an incongruent C–S–H dissolution model was developed. The developed model predicted the release of calcium from C–S–H in sodium chloride solution reasonably and accurately. Further studies are still needed to determine the effect of cation substitution in solid C–S–H on the incongruent dissolution behaviour of C–S–H phases, and to identify mechanisms (e.g., surface complexation) other than cation exchange for the sorption of sodium onto C–S–H and the release of calcium from C–S–H.

References

[1] TRU Coordination Office (Japan Nuclear Cycle Development Institute and The Federation of Electric Power Companies), Progress Report on Disposal Concept for TRU Waste in Japan, JNC TY1400 2000-002, TRU TR-2000-02, March 2000.
[2] U.R. Berner, Evolution of pore water chemistry during degradation of cement in a radioactive waste repository environment, Waste Manage. 12 (1992) 201–219.
[3] A. Atkinson, J.A. Hearne, C.F. Knights, Aqueous chemistry and thermodynamic modelling of $CaO–SiO_2–H_2O$ gels, AERE R 12548, UKAEA, 1987.
[4] S. Börjesson, A. Emrén, 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.
[5] D.A. Kulik, M. Kersten, Aqueous solubility diagrams for cementitious waste stabilization systems: II, end-member stoichiometries of ideal calcium silicate hydrate solid solutions, J. Am. Ceram. Soc. 84 (2001) 3017–3026.
[6] D. Sugiyama, T. Fujita, A thermodynamic model of dissolution and precipitation of calcium silicate hydrates, Cem. Concr. Res. 36 (2006) 227–237.
[7] S.A. Greenberg, T.N. Chang, Solubility relationships in the calcium oxide-silica-water system at 25 °C, J. Phys. Chem. 69 (1965) 182–188.
[8] K. Fujii, W. Kondo, Estimation of thermochemical data for calcium silicate hydrate (C–S–H), J. Am. Ceram. Soc. 66 (1983) C-220–C-221.
[9] K. Fujii, W. Kondo, Heterogeneous equilibrium of calcium silicate hydrate in water at 30 °C, J. Chem. Soc. Dalton Trans. 2 (1981) 645–651.
[10] G.L. Kalousek, Application of differential thermal analysis in a study of the system lime-silica-water, Proc 3rd Int Symp on Chem of Cements, London, 1954, p. 296.
[11] S. Duerden, F.P. Glasser, K. Goldthorpe, J. Pedersen, K. Quillin, D. Ross, S.A. Stronach, M. Tyrer, Chemistry and performance of blended cements and backfills for use in radioactive waste disposal, Mater. Res. Soc. Proc. 465 (1997) 287–294.
[12] M. Atkins, F.P. Glasser, A. Kindness, Cement hydrate phases: solubility at 25 °C, Cem. Concr. Res. 22 (1992) 241–246.
[13] D.L. Parkhurst, C.A.J. Appelo, User's guide to PHREEQC (Version 2)— A computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations, Water-Resources Investigations Report 99-4259, U.S. Geological Survey, 1999.
[14] K.A. Bond, T.G. Heath, C.J. Tweed, HATCHES: A referenced thermodynamic database for chemical equilibrium studies, Nirex Report NSS/R379, 1997.
[15] H.F.W. Taylor, Cement Chemistry, 2nd ed., Thomas Telford Services Ltd., London, 1997, p. 128.
[16] P. Faucon, J.M. Delaye, J. Virlet, J.F. Jacquinot, F. Adenot, Study of the structural properties of the C–S–H(I) by molecular dynamics simulation, Cem. Concr. Res. 27 (1997) 1581–1590.
[17] S.-Y. Hong, F.P. Glasser, Alkali binding in cement pastes Part I. The C–S–H phase, Cem. Concr. Res. 29 (1999) 1893–1903.