Modeling of the Adsorption Behavior of Cs and Sr on Calcium Silicate Hydrates

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Abstract
For safe disposal of the large volume of concrete waste generated during the decommissioning of the Fukushima Daiichi Nuclear Power Station (F1NPS), the state of Cs and Sr contamination in concrete waste must ideally be estimated in advance during waste disposal planning. Cs and Sr are primarily adsorbed by calcium silicate hydrate (C–S–H) in cementitious materials. However, the amount of adsorption varies greatly with the Ca/Si mole ratio (C/S ratio) of C–S–H and with the presence or absence of coexisting elements, both of which vary according to interactions with the environment. This study attempted to model on the results of experiments on Cs and Sr adsorption by synthetic C–S–H with varying C/S ratios. Furthermore, for verifying whether the model can be applied to F1NPS, the results calculated by the model were compared with the experimental results for Cs and Sr adsorption on cement paste subjected to environmental conditions (carbonation, leaching, and presence or absence of coexisting elements (Na, K)). It was confirmed that the present model is overall able to reproduce Cs and Sr adsorption behavior on cement paste, considering changes due to environmental conditions.

1. Introduction
The Fukushima Daiichi Nuclear Power Station (F1NPS) accident that occurred in March 2011 may have resulted in the contamination of concrete structures inside F1NPS by various radionuclides. Safe and rational decommissioning of F1NPS requires that the radionuclide contamination of structures inside the power station be properly evaluated. However, the volume of concrete waste generated during the decommissioning of F1NPS is enormous, and as radionuclides in the concrete structures are subjected to dispersion and inflow/outflow due to external environmental actions over the long period of the decommissioning work, it is not practical to measure directly the contamination status of all concrete structures. Accordingly, during advance planning and the decommissioning work itself, there is a need for technology that will not only ascertain actual measured data concerning contamination conditions but will also, with consideration of the changing nature of the contamination situation, ascertain how the concrete contamination will change in the future - i.e., technology that uses numerical analysis models or other means to predict the future migration of radionuclides. Of the radionuclides contained in the pollution source and the structures to be decommissioned, Cs-137 and Sr-90 are key nuclides owing to their significant radiation effects and long half-lives, and predicting their migration is particularly vital in F1NPS decommissioning. Moreover, as the concrete at F1NPS is thought to be exposed to various environmental actions (including carbonation before and after the accident, leaching (mainly Ca) to stagnant water, retention of contaminated water with varying ion concentrations, and drying before the accident and after the removal of stagnant water) that affect specific areas (Igarashi et al. 2021; Yamada et al. 2021; Kiran et al. 2020, 2021), prediction of the future migration of radionuclides using numerical or other methods must also consider the changes in the condition of the concrete contamination due to interactions with the external environment.

As numerical analysis models, so-called reaction transport model composed of phase equilibrium model between solution and solid phases in concrete and multi-species transport model based on the Nernst-Planck equation (Hosokawa et al. 2011; Nguyen et al. 2006; Johannesson 2000; Samson et al. 1999). The phase equilibrium model that predicts the behavior of Cs and Sr adsorption on cementitious materials can be applied as an
elemental technique for predicting the migration of Cs and Sr in concrete. (Note: A variety of terms, including "sorb," "uptake," "retain," "interaction," "ion exchange," and "binding," appear in the literature; "adsorb" is used in this paper although the detailed "adsorption" mechanisms of Cs and Sr are different.)

Previous reports on the adsorption of various elements on cementitious materials can be summarized as follows. Ochs et al. (2016) reported that calcium silicate hydrates (C–S–H: $\text{xCaO}\cdot\text{ySiO}_2\cdot\text{zH}_2\text{O}$) and aggregate are the primary components with which Cs and Sr interact in concrete. Accordingly, predicting the migration of Cs and Sr in concrete requires modeling of the interaction of Cs and Sr with C–S–H and aggregate. The authors performed and present here this modeling for C–S–H on the basis of experiments involving Cs and Sr adsorption.

The adsorption of Na and K on C–S–H has been reported many times; these elements exist as water-soluble components in pores in hardened cement and are adsorbed on C–S–H competitively with Cs. Researchers have reported that as the Ca/Si mole ratio (C/S) ratio of C–S–H decreases, the amount of Na and K adsorbed on C–S–H increases (Hong and Glasser 1999; Hill et al. 2006; Bach et al. 2013; Myers et al. 2014; Kawabata and Yamada 2015; L'Hôpital et al. 2016). The adsorption amount of Cs, which like Na and K is a monovalent cation, increases in the same manner as that of Na and K when the C/S ratio decreases (Faucon et al. 1997; Haga et al. 2019). The coexistence of Na and K has also been reported to affect the adsorption behavior of Cs because of the competitive adsorption among them (Noshita et al. 2000; Viallis et al. 1999; Viallis-Terrisse 2000; Viallis-Terrisse et al. 2001). Conversely, with regard to divalent Sr, it has been reported that the solid-to-liquid ratio and the C/S ratio of C–S–H as well as the Ca and Sr concentrations in the aqueous phase affect the adsorption of Sr on C–S–H (Tits et al. 2004, 2006; Wieland et al. 2008; Haga et al. 2019). It was further reported that Sr readily carbonates in an atmospheric environment to generate strontianite (SrCO$_3$) when Sr concentration exceeds the solubility of strontianite (SrH$_2$O) and it replaces Ca in other hydrates such as calcite (CaCO$_3$) and ettringite (3CaOAl$_2$O$_3$·3CaSO$_4$·32H$_2$O) (Tits et al. 2004; Haga et al. 2019). As noted above, the composition of C–S–H has an effect on the adsorption of elements on C–S–H. However, many researchers have reported that the composition of C–S–H changes with the condition of materials, such as the type of Portland cement and the cement to supplemental cementitious materials ratio, as well as with environmental actions such as carbonation and leaching (Nishikawa and Suzuki 1994; Haga et al. 2005; Black et al. 2008; Jain and Neithalath 2009; Sevelsted and Skibsted 2015). For those reasons, the interaction of C–S–H with Cs and Sr requires a model that is able to consider changes in the C/S ratio of C–S–H as well as the presence or absence of coexisting elements and their concentrations. As these behaviors are considered to be governed by thermodynamic phase equilibrium, a model based on thermodynamic phase equilibrium is adopted in this study.

Modeling the interaction of C–S–H with Cs and Sr based on thermodynamic phase equilibrium requires first modeling the dissolution and precipitation behavior of C–S–H in terms of thermodynamic phase equilibrium. A typical model of the dissolution and precipitation behavior of C–S–H considers C–S–H as a solid solution composed of multiple end members, as exemplified by Atkins (1992). By contrast, the C–S–H model proposed by Nonat (2004) does not assume C–S–H to be a solid solution, but models the dissolution and precipitation behavior of C–S–H using the dissolution equilibrium of the silicate dimers that compose the layered silicate in C–S–H and the surface complex reaction of the silanol sites (–SiOH) on the layered silicate. Modeling of the adsorption of Cs, Na, and K on C–S–H is often expressed using a surface complex model in which these elements react with silanol sites on the C–S–H surface (Heath et al. 1996; Pointeau 2000; Viallis-Terrisse 2000; Viallis-Terrisse et al. 2001; Henocq 2005, 2017; Ochs et al. 2006; Plusquellec 2014). Accordingly, the authors decided to model the interaction of C–S–H with Cs and Sr based on thermodynamic phase equilibrium using Nonat's C–S–H model, which has a high affinity with the surface complex model. However, as Sr is known to be adsorbed through ion exchange with Ca (Tits et al. 2004, 2006; Wieland et al. 2008), Kulik et al. (2007) proposed a solid solution model for Sr adsorption by C–S–H. To address such ion exchange, the authors modeled the ion exchange between Sr and Ca within the framework of a surface complex reaction.

Based on the above, in this study, the interaction of C–S–H with Cs and Sr was modeled through thermodynamic phase equilibrium using the experimental results of Haga et al. (2019) for Cs and Sr adsorption on synthetic C–S–H under varied C/S ratios. Next, the authors incorporated the constructed model in the calculation of the phase composition of cement paste based on thermodynamic phase equilibrium and attempted to reproduce the adsorption behavior of Cs and Sr on cementitious materials. The objective was to reproduce the experiment of Haga et al. (2019) on Cs and Sr adsorption by cement paste. In this experiment, the effects of Na and K in cement and those of carbonation or leaching on the adsorption behavior were observed. External environmental actions, including carbonation and leaching due to contact with stagnant water, have affected some areas of the concrete structure of F1NPS. These external environmental actions were investigated on the assumption that they affect the adsorption behavior of Cs and Sr in cementitious materials. The model in this study can also be used for determining the presence of Na and K in cement as well as external environmental actions such as carbonation and leaching, because the model calculates the composition of cement paste based on thermodynamic phase equilibrium. Accordingly, using the ex-
Experimental results of Haga et al. (2019) for Cs and Sr adsorption by cement paste, the authors investigated whether the model constructed in this study can reproduce the adsorption behavior of Cs and Sr on cementitious materials in the presence of Na and K and considering the effects of external environment action. Subsequently, the validity of the constructed model is evaluated.

2. Modeling of interaction of C–S–H with Cs and Sr ions

In this section, the interaction of Cs and Sr with C–S–H is modeled through thermodynamic phase equilibrium using the results of the experiment conducted by Haga et al. (2019) for the adsorption of Cs and Sr by synthetic C–S–H under varying C/S ratios.

2.1 Reference experiment

Haga et al. (2019) synthesized C-S-H at four C/S ratios (0.6, 0.8, 1.0, 1.2). It should be noted that the C/S ratio in their experiment of is calculated from the chemical composition of the entire synthesized solid phase, and may contain mineral phases other than C-S-H. They immersed synthetic C–S–H for seven days in an aqueous solution with a liquid-to-solid ratio of 10:1, prepared at specified concentrations (1×10^{-7} to 1×10^{0} mol/L) using chlorides of radioactive and/or stable Cs and Sr nuclides and ion-exchanged water. They measured the amounts of Cs and Sr adsorbed on the synthetic C–S–H on the basis of the change in the concentration of the aqueous solution before and after immersion (Fig. 1). The amount of Cs adsorbed on synthetic C–S–H was found to increase as the C/S ratio in C–S–H decreased, as shown in Fig. 1. The results regarding the adsorption behavior of Cs on C–S–H with varying C/S ratios are consistent with the results reported by Noshita et al. (2000) and Ochs et al. (2006). Conversely, the C/S ratio of C–S–H was found to have nearly no effect on the adsorption of Sr on C–S–H, which suggests a difference between the adsorption behaviors of Sr and Cs on C–S–H. In addition to Haga et al. (2019), some other studies examined the adsorption of Sr on C–S–H. Among these, Tits et al. (2004) conducted experiments on the adsorption of Sr on C–S–H in artificial pore water of cement paste (pH=13.3) and reported that the amount of Sr adsorbed increased as the C/S ratio of the C–S–H decreased. Subsequently, Tits et al. (2006) indicated that the higher the Ca concentration in the liquid phase, the lower the amount of Sr adsorbed. However, in case of C–S–H with a low C/S ratio in concrete in real environments, it is unlikely that the pH of water in pores will be high, as seen in the experimental conditions of Tits et al. (2006) because everything is in equilibrium and pH, C/S ratio of C-S-H, and Ca concentration interact each other. Based on the above, this study performed modeling based on the experimental results of Haga et al. (2019), who used ion-exchanged water to prepare aqueous solutions of Cs and Sr.

The concentration of radioactive contamination in typical stagnant water at F1NPS was 1.3×10^{-5} mol/L for Cs and 3.4×10^{-6} mol/L for Sr at the initial stage of the incident. However, with the progress of decontamination, it was reported that the concentrations of Cs and Sr were approximately 1.8×10^{-6} mol/L and 6.6×10^{-8} mol/L, respectively (Nagoya University 2018). In this way, although the concentrations of radioactive Cs and Sr in existing stagnant water differ by an order of two magnitudes, as the stagnant water contains seawater components due to the tsunami or in groundwater, and as the seawater contains approximately 8.9×10^{-5} mol/L of stable Sr (Nozaki 1997), the range of Cs and Sr concentrations in the stagnant water can be assumed to be approximately 10^{-7} to 10^{-6} mol/L. Accordingly, the range of the experimental standard of Haga et al. (2019) encompasses the typical concentration of stagnant water at F1NPS.

2.2 Thermodynamic equilibrium model of C–S–H

In modeling the interaction of C–S–H with Cs and Sr, this study implemented the C–S–H dissolution and precipitation equilibrium model of Nonat (2004) on PHREEQC and used a thermodynamic phase equilibrium model that calculates the composition and the produced amount of C–S–H based on phase equilibrium
theory. The C–S–H dissolution and precipitation equilibrium model of Nonat et al. consists of multiple reaction equations pertaining to the dissolution reaction of the silicate dimer that constitutes the layered silicate structure in C–S–H and the silanol site –SiOH reaction of the layered silicate, with thermodynamic equilibrium constants given for each reaction equation. The C–S–H surface is charged through the ionization of silanol sites and an electric double layer (EDL) is formed. The Nonat model (Nonat 2004) assumes that the C–S–H surface electric potential and the electric charge distribution within the EDL are governed by the Poisson–Boltzmann equation; thus, solving this equation will give with the composition of the EDL. Meanwhile, the composition of the liquid phase that excludes the EDL and the type and amount of the solid phase that is formed are calculated on the basis of phase equilibrium theory.

Table 1 shows the C–S–H reaction equations and their log K values used in the model. Solubility of C–S–H represents a pairing site. “C–S–H internal and external surface sites” represents what the silanol group at the pairing site is attached to. In other words, it can calculate increase/decrease in Ca and Si of C–S–H, and present of bridging site. Therefore, we can use Table 1 to simulate C–S–H of varying C/S ratios. The chemical species of the liquid phase (except those used here), the reaction equations for the solid phase, and log K for each reaction equation are described in the database WATEQ4F (USGS 2005) attributed to PHREEQC.

It has been reported in recent years that C–S–H exists as calcium aluminosilicate hydrate (C–A–S–H: wCaO-xAl2O3-ySiO2-zH2O) in which some SiO2 is replaced by Al2O3 (Andersen et al. 2006; Sun et al. 2006; Manzano et al. 2009; Pardal 2012; Richardson 2014; Haas and Nonat 2015; Lothenbach and Nonat 2015). Some of these studies modeled the adsorption behavior of Na and K on C–A–S–H and reported that the amount of adsorption of monovalent cations increases with the entry of Al into C–S–H (Hosokawa et al. 2019). In addition, Minato et al. (2015) evaluated the adsorption behavior of Cs and reported that the amount of Cs adsorbed on C–A–S–H is higher than that adsorbed on C–S–H. In view of the later findings, it is thus reasonable to model the adsorption behavior of Cs and Sr on C–A–S–H rather than on C–S–H. However, sufficient experimental data regarding the adsorption of Cs and Sr on C–A–S–H has not yet been provided, and Haga et al. (2019) reported that the skeletal structure of C–A–S–H changes with adsorption test conditions. As it is necessary to model the structural change in C–A–S–H itself before modeling the adsorption behavior of ions on C–A–S–H, this study considers the adsorption behavior of Cs and Sr on C–S–H as the subject of its modeling rather than on C–A–S–H, which is a task for the future.

2.3 Determining log K for the Cs and Sr ions adsorbed by C–S–H

In modeling the interaction of C–S–H with Cs and Sr, this study assumed that the adsorption of Cs and Sr by C–S–H occurs due to the surface complex reaction between the silanol sites of C–S–H and Cs and Sr ions (Fig. 2). Accordingly, based on the surface complex reaction equation reported by Hosokawa et al. (2019) to express the adsorption of Na and K on C–S–H, the surface complex reaction equations for adsorption of Cs and Sr by the silanol sites of C–S–H were formulated as shown in Table 2, and these reaction equations and their equilibrium constants (log K) were introduced into PHREEQC, in which the C–S–H dissolution and precipitation equi-

### Table 1 Dissolution reactions and log K of C–S–H at 25°C (Nonat 2004).

| Phase                        | Reaction equation                                                      | log K  |
|------------------------------|------------------------------------------------------------------------|--------|
| C–S–H particle               | Ca3Si2O5H4 + 4H+ + H2O = 2Ca2+ + 2H2SiO4                                | 29.6   |
| C–S–H internal and external surface sites | –SiOH = –SiO− + H+                                                  | −11.8  |
|                              | –SiOH + Ca2+ = –SiOCa2+ + H+                                            | −9.0   |
|                              | –SiOH + –SiOH + Ca2+ = –SiOCaSiO− + 2H+                                | −20.4  |
|                              | –SiOH + Ca2+ + H2O = –SiOCaOH + 2H+                                   | −24.85 |
|                              | –SiOH + –SiOH + H2SiO4 = –SiOSi(OH)2SiO− + 2H2O                        | 7.0    |

### Table 2 Considered interaction of Cs and Sr with C–S–H.

| Reaction equation                                         | log K  |
|-----------------------------------------------------------|--------|
| −SiOH + Cs+ = −SiOCS+ + H+                                | log Kcs |
| −SiOSi2OH + Cs+ = −SiOSi2OCs + H+                         | log Kcs |
| −SiOH + Sr2+ = −SiOSr+ + H+                               | log Ksr(1) |
| −SiOSi2OH + Sr2+ = −SiOSi2OSr+ + H+                       | log Ksr(1) |
| −SiOH + 0.5Sr2+ = −SiOSr− + H+                            | log Ksr(2) |
| −SiOSi2OH + 0.5Sr2+ = −SiOSi2OSr− + H+                    | log Ksr(2) |

<Example>

![Fig. 2 Schematic diagram of the ion exchange reaction at the silanol sites of C–S–H.](image-url)
The equilibrium model of Nonat (2004) was implemented. Furthermore, this formulation of the Cs and Sr adsorption reaction equations serves to formulate the ion exchange reactions between these ions. As an example, the ion exchange reaction between Na and Cs in silanol sites can be derived from Eqs. (1) and (2) as Eq (3).

\[
\text{SiOH} + \text{Na}^+ \rightarrow \text{SiONa} + \text{H}^+ \quad (1)
\]

\[
\text{SiOH} + \text{Cs}^+ \rightarrow \text{SiOCs} + \text{H}^+ \quad (2)
\]

\[
\text{SiONa} + \text{Cs}^+ \rightarrow \text{SiOCs} + \text{Na}^+ \quad (3)
\]

In Table 2, four reaction equations for Sr and silanol sites are defined to express the ion exchange reactions of Ca and Sr with silanol sites. Stated differently, the ion exchange reactions of Ca\(^{2+}\) and Sr\(^{2+}\) with the silanol sites were formulated by defining for Sr\(^{2+}\) in Table 2 the same type of reaction equations shown in Table 1 for silanol sites and Ca\(^{2+}\).

The log \(K\) values of the formulated surface complex reaction equations were obtained through a least squares method described below, using the adsorption experiment results of Haga et al. (2019). First, appropriate initial values were given to log \(K\). Using PHREEQC, the liquid phase composition after adsorption experiment was then calculated from the mass and chemical composition of C–S–H and the volume and initial concentration of the liquid phase; then, the difference (error) between the liquid phase composition before and after the adsorption testing of Haga et al. (2019) was calculated as follows:

\[
\text{Error} = (\log(A) - \log(B))^2 \quad (4)
\]

where \(A\) is the concentration after adsorption as obtained in the experiment (Haga et al. 2019) and \(B\) is the concentration after adsorption obtained by our calculation.

Next, the errors were calculated for all initial liquid phase concentrations using the same method, and the sum of the errors was calculated for all initial liquid phase concentrations. The same calculation was performed multiple times with varying log \(K\); then, log \(K\) for the smallest sum of errors was set as log \(K\) for this study. The reason for errors being calculated for the logarithms of \(A\) and \(B\) is that the range of the initial liquid phase concentrations is extremely wide (1×10\(^{-7}\) to 1×10\(^{0}\) mol/L), as shown in Fig. 1. Table 3 shows log \(K\) set through the above method for all levels of adsorption testing. In this way, log \(K\) values of the surface complex reactions of Cs and Sr with silanol sites were assigned according to the C/S ratios of C–S–H. As is well known, there are two kinds of silanol sites in C-S-H, which is the anionic group reacting with cations. To express these different silanol sites on C-S-H, we set two reactions for Cs and Sr. “-SiOH” expresses adsorption by a pairing site. While, “-SiOSi\(_{0.5}\)OH” expresses adsorption by a bridging site. But the same log \(K\) is given in the model calculation since data to differentiate the reactivity of those sites are not available.

Figure 3 shows the calculated results for the amount of Cs and Sr adsorbed by C–S–H with log \(K\) values of the surface complex reaction equations for silanol sites and Cs and Sr taken from Table 3 plotted against the experimental results used to set log \(K\) values. The calculated and experimental results for the amount of Sr adsorbed by C–S–H were nearly identical. For Cs, when the C/S ratio of C–S–H was 0.6, 0.8, and 1.0, the calculated amount tended to be larger than the experimental amount, which was 10\(^{-1}\) mol/kg or higher. We think this is due to the change in the adsorption amounts depending on the concentration of Cs is larger than that of Sr. In the experiment of Haga et al. (2019), in the case of C-S-H (C/S=0.6), the distribution ratio (Rd) is 45.5 L/kg at initial Cs concentration 10\(^{-2}\) M, while it is 1001.5 L/kg at initial concentration 10\(^{-6}\) M. However, in the case of Sr, Rd is 32.0 L/kg at initial Cs concentration 10\(^{-2}\) M, while

| C/S of C–S–H | log \(K_{cs}\) | log \(K_{sr(1)}\) | log \(K_{sr(2)}\) |
|------------|----------------|----------------|----------------|
| 1.2        | -12.75         | -9.32          | -12.1          |
| 1.0        | -10.48         | -8.76          | -18.6          |
| 0.8        | -9.29          | -8.47          | -14.4          |
| 0.6        | -8.35          | -7.71          | -13.2          |

![Fig. 3 Comparison of experimental and calculated amount of Cs and Sr adsorbed by C–S–H [modified from Haga et al. (2019)].](image-url)
it is 334.7 L/kg at initial concentration 10^{-6} M. It is very difficult to completely fit this data, we set the log $K$ produced the smallest errors in this report. The experimental results and the calculated results did not completely match, but they were on the same order. From the above, the authors considered that a model that reproduces the adsorption of Cs and Sr by C–S–H has been constructed.

### 3. Reproduction of the interaction of cement paste with Cs and Sr using the constructed model

In this section, the authors incorporated the constructed model of the interaction of C–S–H with Cs and Sr into a model that calculates the phase composition of cement pastes based on the thermodynamic phase equilibrium and attempted to reproduce the adsorption behavior of Cs and Sr on cementitious materials. As the target for reproduction, the study considered the experiment performed by Haga et al. (2019) on Cs and Sr adsorption by cement pastes. In the experiment, the effects of Na and K in cement on the adsorption behavior of Cs and Sr, along with the effects of external environmental actions such as carbonation and leaching, were taken into account to test the adsorption behavior by cement pastes. In this section, the adsorption behavior of Cs and Sr on cementitious materials is reproduced by considering the effects of Na and K in cement and those of external environmental actions. Further, the validity of the constructed model is verified.

#### 3.1 Reference experiment

An outline of the experiment by Haga et al. (2019) on the adsorption of Cs and Sr by cement paste is provided here. In the experiment, cement paste with a water-to-cement ratio of 0.5 was mixed and molded into a specified shape using ion-exchanged water and ordinary Portland cement (OPC). The cement paste samples were sealed and cured at 20°C, 60% RH, and 5% CO$_2$ concentration. Next, to consider the effects of leaching on the adsorption of the cement paste, the washed samples in which only Ca is present as cation were subjected to accelerated leaching for Ca using ammonium nitrate. Similar adsorption experiments were conducted on both types of samples.

The OPC used to prepare the cement paste samples and the chemical composition of each cement paste sample measured by X-ray fluorescence analysis and thermal analysis are shown in Table 4. The amounts of each element adsorbed by the cement paste samples following the adsorption experiment are shown in Figs. 4 to 6. Results are shown for the initial liquid phase concentration of 1×10^{-5}, 1×10^{-4} mol/L for the Cs only case and the initial phase concentration of 1×10^{-5} mol/L for the Cs+Na, K case in Figs. 4, or for the initial liquid phase concentration of 1×10^{-4} mol/L for Na in washed samples in Fig. 6. This is because the amounts of adsorption were below the detection limit. Moreover, among the levels of Cs+Na, K, the Na and K adsorption amount when the initial liquid phase concentration of Cs was 1×10^{-2} mol/L was not measured, and thus is not shown in Fig. 6.

As shown in Table 4, in contrast to Na$_2$O concentration of 0.3 mass% and K$_2$O concentration of 0.5 mass% in the raw material OPC, both their concentrations were reduced to 0.0% mass in the washed, carbonated, and leached samples, and Na and K were removed. The chemical composition of the carbonated samples contained CO$_2$; carbonates including hemicarbonate (7CaO·2Al$_2$O$_3$·CaCO$_3$·24H$_2$O), calcite (CaCO$_3$), vaterite (CaCO$_3$), and aragonite (CaCO$_3$) were confirmed through X-Ray Diffraction (XRD). Conversely, the

| Chemical composition (mass %) |
|------------------------------|
| OPC | Washed | Carbonated | Leached |
| SiO$_2$ | 21.1 | 17.9 | 14.3 | 29.2 |
| Al$_2$O$_3$ | 5.4 | 4.6 | 3.6 | 7.8 |
| Fe$_2$O$_3$ | 2.9 | 2.5 | 2.0 | 4.2 |
| CaO | 64.8 | 49.5 | 39.4 | 31.4 |
| MgO | 1.5 | 1.5 | 1.2 | 2.4 |
| SO$_3$ | 2.0 | 1.4 | 1.1 | 1.0 |
| Na$_2$O | 0.3 | 0.0 | 0.0 | 0.0 |
| K$_2$O | 0.5 | 0.0 | 0.0 | 0.0 |
| TiO$_2$ | 0.3 | 0.2 | 0.2 | 0.4 |
| P$_2$O$_5$ | 0.1 | 0.2 | 0.1 | 0.3 |
| MnO | 0.1 | 0.0 | 0.0 | 0.1 |
| H$_2$O | 0.7 | 22.1 | 14.5 | 23.3 |
| CO$_2$ | N.D. | N.D. | 23.4 | N.D. |
| etc. | 0.3 | 0.0 | 0.0 | 0.0 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 |
leached sample had a lower CaO concentration, higher SiO₂ concentration, and suggesting lower C/S ratio than the other samples.

Figures 4 to 6 show that the adsorption amounts in the carbonated and leached samples are 1 to 2 orders of magnitude higher than the adsorption amount in the washed sample. This is because carbonation and leaching decrease the C/S ratio in C–S–H, resulting in an increase

![Graphs showing Cs adsorption amounts](image)

![Graphs showing Sr adsorption amounts](image)

![Graphs showing Na and K adsorption amounts](image)
in the proportion of negatively charged silanol sites in C–S–H, a decrease in the surface potential of C–S–H, and an increase in the cation adsorption capacity in the cement paste. Furthermore, carbonated and leached samples may be producing the alumina silica gel by dissolving C–S–H. The alumina silica gel is considered to increase the cation adsorption capacity. This will be discussed later.

As can be seen from Fig. 6, not only the adsorption amounts of Cs and Sr but also the adsorption amounts of Na and K is increasing. Therefore, to reiterate, the experimental results of Haga et al. (2019) show that a model predicting Cs and Sr migration in concrete must take into account the transformed states of these and the effects of coexisting elements.

### 3.2 Thermodynamic equilibrium model to calculate the phase assemblage of cement paste

To use the authors' model to reproduce the experiment of Haga et al. (2019) on the adsorption of Cs and Sr on cement paste as outlined in the previous section, the model of the interaction of C–S–H with Cs and Sr constructed in Section 2 was incorporated into a model that calculates the phase composition of cement paste on the basis of the thermodynamic phase equilibrium (Hosokawa et al. 2011), which is also constructed on PHREEQC similar to the model of the interaction of C–S–H with Cs and Sr. The dissolution reaction equations for minerals other than the C–S–H used in the model and their equilibrium constants are shown in Table 5. In this model, the change in cement phase due to carbonation and leaching was calculated as the formation of minerals shown in Table 5 and the decrease in C/S of C-S-H. To calculate the interaction of C–S–H with Na and K, this study used the model of Hosokawa et al. (2019), which calculates this as a surface complex reaction of silanol sites on C–S–H with Na and K in the same manner as the model of interaction of C–S–H with Cs and Sr. The surface complex reaction equations for silanol sites with Na and K and their equilibrium constants are shown in Table 6.

### Table 5 Dissolution reactions and log K of minerals (25°C).

| Phase          | Reaction equation                                                                 | log K  | Ref. |
|----------------|-----------------------------------------------------------------------------------|--------|------|
| Portlandite    | Ca(OH)₂ + 2H⁺ = Ca²⁺ + 2H₂O                                                        | 22.8   | a    |
| Gypsum         | CaSO₄ · 2H₂O = Ca²⁺ + SO₄²⁻ + 2H₂O                                                | -4.58  | a    |
| Ettringite     | Ca₃(Al₅(PO₄)₃)(OH)₆ · 26H₂O = 2Al(OH)₆⁻ + 6Ca²⁺ + 26H₂O + 4OH⁻ + 3SO₄²⁻         | -45.09 | b    |
| Monocarbonate  | (CaO)₂(Al₂O₃)·Ca·11H₂O = 4Ca²⁺ + 2Al(OH)₆⁻ + CO₃²⁻ + 4OH⁻ + 5H₂O                 | -31.47 | b    |
| Calcite        | CaCO₃ + H⁺ = Ca²⁺ + HCO₃⁻                                                          | 1.849  | b    |
| Brucite        | Mg(OH)₂ + 2H⁺ = Mg²⁺ + 2H₂O                                                       | 16.84  | a    |
| Al(OH)₃        | Al(OH)₃ + OH⁻ = Al(OH)₄                                                            | 0.24   | b    |
| Fe(OH)₃        | Fe(OH)₃ + 3H⁺ = Fe³⁺ + 3H₂O                                                       | 5.00   | b    |
| C₃ASH₄         | (CaO)₃Al₂O₅SiO₂ · 4H₂O + 12H⁺ = 8H₂O + 2Al³⁺ + 3Ca²⁺ + H₃SiO₄                     | 71.17  | c    |
| C₄AH₁₃        | (CaO)₄Al₂O₄ · 13H₂O = 4Ca²⁺ + 2Al(OH)₆⁻ + 6OH⁻ + 6H₂O                            | -25.56 | b    |
| Friedel’s salt | Ca₃Al₂Cl₄(OH)₁₂ · 4H₂O = 4Ca²⁺ + 2Al(OH)₆⁻ + 2Cl⁻ + 4OH⁻ + 4H₂O                 | -27.3  | d    |
| SiO₂ (amorphous) | SiO₂ + 2H₂O = H₂SiO₄                                                              | -2.71  | a    |

### Table 6 Reaction equations of silanol sites with Na and K and their log K (Hosokawa et al. 2019).

| Reaction equation                                                                 | log K  |
|-----------------------------------------------------------------------------------|--------|
| –SiOH + Na⁺ = –SiONA⁺ + H⁺                                                       | -12.1  |
| –SiOSi₃OSiOH + Na⁺ = –SiOSi₆OSiONa + H⁺                                            | -11.4  |
| –SiOH + K⁺ = –SiOK + H⁺                                                         | -11.9  |
| –SiOSi₆OSiOH + K⁺ = –SiOSi₆OSiOK + H⁺                                            | -10.9  |

a: USGS (2005), b: Lothenbach and Winnefeld (2006), c: Thermoddem (2020), d: Loser et al. (2010)
and they were fed into the model that calculates the phase composition of cement paste. The initial C/S ratio was varied and the calculation was repeated until the C/S ratio of C–S–H obtained after the phase equilibrium calculation matched the initial C/S ratio in order to derive the optimal equilibrium constant for each sample. Thus, the study sought to reproduce the experiment of Haga et al. (2019).

3.3 Calculation results and discussion
Table 7 shows the summary of experimental conditions and the corresponding C/S ratios of C–S–H obtained by using PHREEQC to reproduce the experiment of Haga et al. (2019).

For any type of aqueous solution in which cement paste samples were immersed, the C/S ratio of C–S–H in the washed sample was calculated to be approximately 1.3. The C/S ratio of C–S–H in general OPC paste has often been reported to be greater than 1.5; the ratio of 1.3 calculated under this model is lower than such commonly reported values, because the amounts of Na and K in the washed sample reduced through washing, resulting in a lower pH in the aqueous solution after equilibration compared with that in the general case. In other words, the reduction in pH is considered to increase the solubility of calcium, resulting in a lower calculated C/S ratio of C–S–H.

By contrast, the calculated C/S ratios in the cases of carbonated and leached cement paste samples were 0.7 to 0.8, lower than that in the washed samples. Further, in the carbonated and leached samples, the C/S ratio increased somewhat when Na and K coexisted in the aqueous solution or when the concentration of Cs was high. It is likely that in the carbonated samples, the Ca in C–S–H was consumed in the carbonation reaction, thus decreasing the C/S ratio, whereas in the leached samples, Ca was drawn out of the cement paste through leaching, which decreased the C/S ratio. In either case, however, it was considered that the model reproduced, through calculation, the phenomena by which the respective C/S ratios decreased. Regarding the phenomenon by which the C/S ratio increased slightly when Na and K coexisted or when the concentration of Cs was high, it was considered that this occurred because the pH of the aqueous solution after equilibrium increased and the solubility of calcium decreased due to high concentrations of Na, K, and Cs (10^{-3} mol/L).

The calculated results of the amounts of Cs adsorption by cement paste samples obtained by reproducing the adsorption test of Cs and Sr on cement pastes using PHREEQC based on thermodynamic phase equilibrium, the calculated results for Sr, and those for Na and K adsorption amounts are plotted against experimental results in Figs. 7 to 9, respectively. Although, some data points listed in Table 7 weren't plotted in Fig. 7 because the Cs concentration was below the detection limit in the experiments, it is possible to obtain the calculated adsorption amounts of Cs, such as on washed OPC for Cs only were 4.5×10^{-4} mol/kg at the initial Cs concentration 10^{-5} mol/L, and 3.2×10^{-2} mol/kg at initial Cs concentration 10^{-7} mol/L, and the calculated adsorption amount of Cs on washed OPC for Cs+Na, K 0.1M was 2.4×10^{-4} mol/kg at the initial Cs concentration 10^{-5} mol. The corresponding values could not be obtained by experiments because they were below the detection limit. But it is possible to obtain the values by simulation, which is the one of the merits of the simulation.

Regarding the adsorption amounts of Cs and Sr, the results calculated by the model and those obtained by the experiment were nearly identical in all cases as shown in Figs. 7 and 8. In the immersion test in which Cs and Sr are 10^{-3} mol/L, Cs is estimated to be relatively high and Sr is estimated to be low in carbonated sample and leached sample. As can be seen from Fig. 3, the adsorption amounts of Cs is overestimated at high concentration in this model, and it is considered that Sr is underestimated in the Cs and Sr coexistence system due to the influence of coexistence. The experimental results and the calculated results did not completely match, but they were on the same order. Thus, it was shown that, even when Na and K coexist in an aqueous solution of Cs and even under the effect of external environment action such as carbonation or leaching, this model is able to reproduce the adsorption behavior of Cs and Sr by cement paste by considering these effects through the use of phase equilibrium calculation.

| Type of solution | Initial Concentration (mol/L) | C/S ratio of C–S–H |
|-----------------|------------------------------|--------------------|
| Cs only         | Cs: 1×10^{-3} Sr: - Na: - K: - Cl: 1×10^{-3} | Washed: 0.69 Carbonated: 0.76 Leached: 0.76 |
| Cs/Sr=1         | Cs: 1×10^{-3} Sr: 1×10^{-3} Na: - K: - Cl: 1×10^{-3} | Washed: 0.69 Carbonated: 0.76 Leached: 0.76 |
| Cs+Na,K         | Cs: 1×10^{-1} Na: 3×10^{-1} K: - Cl: 3×10^{-1} | Washed: 0.69 Carbonated: 0.76 Leached: 0.76 |

"-" means not included or not measured.
Conversely, with regard to the adsorption amounts of Na and K, in some cases, the differences between experimental and calculated results were large as shown in Fig. 9. In cases of carbonated samples or leached samples in particular, the differences between experimental and calculated results were noteworthy. The model of the interaction of C–S–H with Na and K used in this study is
a pre-existing model and was not constructed in this study. However, considering that the absorption amounts of Na and K have a large effect on the pH of water in pores in cement paste, it was thought that the model of the interaction of C–S–H with Na and K, especially under carbonation or leaching effects, require re-examination in the future. As noted above, even under the coexistence of Na and K, the calculated results of the adsorption amount of Cs under this model were found to be in good agreement with experimental results. Accordingly, even if the model of the interaction of C–S–H with Na and K is reconstructed and introduced into this model in the future, it will have no effect on the calculated results for the adsorption amount of Cs.

Based on the above, the model constructed in this study to reproduce the adsorption of Cs and Sr by cement paste was considered to be valid for F1NPS decommisioning plans as an elemental technology that uses numerical calculations to predict the migration of Cs and Sr in the sections of contaminated concrete that have been subjected to various external environmental actions.

### 3.4 Future issues to address in bringing the model of this study closer to actual phenomena

As described in the previous section, the differences between calculated and experimental results for the amounts of Na and K adsorbed by cement paste were large, particularly in the cases of carbonated and leached samples. However, according to previous reports, structural changes of C–S–H may occur due to the action of carbonation or leaching, which are not considered by this study's model of the adsorption behavior of C–S–H. Other phenomena that are expected to occur in actual concrete are also not considered in the present model. This section considers future issues pertaining to this study's model in order to bring predictions of Cs and Sr migration in the contaminated concrete of F1NPS closer to the actual phenomena.

Haga et al. (2019) used $^{29}$Si Magic Angle Spinning-Nuclear Magnetic Resonance (MAS-NMR) and $^{27}$Al MAS-NMR to analyze the structure of C–S–H in washed, carbonated, and leached cement paste samples, and reported the following results. According to the analysis of $^{29}$Si MAS-NMR, although the Q$^0$, Q$^1$, and Q$^2$ structures of the silicate complex can be confirmed in washed cement paste, the Q$^3$ and Q$^4$ structures, which could not be observed in washed cement paste, were the major constituents in carbonated cement paste, with decreased percentage of Q$^1$. Q$^2$ indicates the end of the silicate chain in C–S–H or the presence of a silicate dimer. For this reason, according to Haga et al. (2019), C–S–H is presumed to have decomposed through carbonation into calcium carbonate and into amorphous silica having Q$^2$ and Q$^4$ structures. In addition, based on the $^{27}$Al MAS-NMR analysis, Haga et al. (2019) estimated that this amorphous silica structure contains Al of 4-coordinates in the form of alumina silica gel. The Al of 4-coordinate was increased by carbonation significantly with the simultaneous reduction of Al of 6-coordinate of Ca aluminates. The amount of alumina silica gel was found to be less in leached cement paste than in carbonated cement paste. This formation of alumina silica gel was considered to be caused by the decomposition of C–S–H and Ca aluminate hydrates by the leaching of Ca.

Besides, the exchanging reaction of silicate tetrahedra and aluminate tetrahedra requires charge balance for aluminate to accompany monovalent ion such as alkali metals.

Results of the NMR analysis of carbonated cementitious materials have also been reported by Groves et al. (1991) and Sevelsted and Skibsted (2015). Groves et al. (1991) reported that amorphous silica with Q$^3$ and Q$^4$ structures was formed in 16-hour accelerated carbonated C3S paste. The results of Haga et al. (2019), which address cement paste carbonated under accelerated conditions, are generally close to the analytical results of Groves et al. (1991). While it is possible that the structural change of C–S–H in the case of accelerated carbonation differs from that in case of carbonation in an actual environment, Sevelsted and Skibsted (2015) reported that, 12-week atmospheric exposure of synthetic C–S–H with varied C/S ratios (C/S=0.66, 1.00, 1.50) resulted in alumina silica gel was formed in all of the synthetic C–S–H. Accordingly, it can be considered highly likely that alumina silica gel is also produced in concrete that is subjected to atmospheric exposure for a long period of time.

With regard to Sr, the model in this study only considers interaction with C–S–H. Conversely, in the experiment of Haga et al. (2019) on Sr adsorption by cementitious hydrates and carbonate minerals, it was found that apart from C–S–H, calcite (CaCO$_3$), ettringite (3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O), and monocarbonate (3CaO·Al$_2$O$_3$·CaCO$_3$·11H$_2$O) are minerals that adsorb Sr when Sr concentration in the aqueous solution is high (1×10$^2$ mol/L). Accordingly, it can be considered necessary to consider the interaction of Sr with carbonates and hydrates other than C–S–H.

In the model constructed in this study, the formation of calcite and the decrease in the C/S ratio of C–S–H due to carbonation and leaching were calculated, and the interaction between C–S–H and ions was quantitatively evaluated based on the decreased C/S ratio. As noted earlier, however, in actual conditions, alumina silica gel is formed from C–S–H and Ca aluminate hydrates through carbonation or leaching and it is likely that it interacts with ions and that Sr interacts with hydrates other than C–S–H. Judging from the Q$^3$ of carbonated cement hydrates, alkali silica gel is expected to also be produced. Moreover, in real cement paste, significant amounts of Al are included in C–S–H as C–A–S–H and the Al content in C–A–S–H is affected by the alkali concentration of coexisting solution as reported by Haga et al. (2019). From $^{27}$Al MAS-NMR analysis, when the alkali concentration of coexisting solution is high, the Al/Si ratio of C–A–S–H increases. Therefore, more ad-
vanced model considering Al in C–A–S–H is also important. The model largely reproduces the adsorption behavior of Cs and Sr on cement paste altered by external environmental actions and is considered to be applicable to predict the migration of Cs and Sr in contaminated concrete at F1NPS. However, if the future objective is to bring the prediction of Cs and Sr migration closer to the actual phenomena, the issues to address in future are modeling of the structural changes in C–S–H due to external environmental action and the resulting adsorption of ions by alumina silica gel, modeling of the adsorption of Sr by calcites and hydrates other than C–S–H and aggregate, and incorporation of these into this study’s model to calculate the phase composition of cement paste.

4. Conclusions

This study investigated the construction of a model that reproduces the adsorption of Cs and Sr by cement paste, as an elemental technique that uses numerical calculations to predict the migration of Cs and Sr in areas of contaminated concrete affected by various external environmental actions. The model is intended for use in F1NPS decommissioning plans. Cs and Sr are adsorbed by mainly C–S–H among all the hydrates that constitute cement paste; C–S–H exhibits an adsorption capacity that varies with its C/S ratio. Based on this fact and the thermodynamic phase equilibrium, the authors constructed a model of Cs and Sr adsorption by C–S–H by taking into consideration changes in C–S–H. This C–S–H model was then incorporated into a model of thermodynamic phase equilibrium to predict the phase composition of cement paste, and then the Cs and Sr adsorption behavior on cement paste was reproduced. The results obtained are summarized below.

1. To model the interaction of C–S–H with Cs and Sr on the basis of the thermodynamic phase equilibrium, the adsorption of Cs and Sr by C–S–H was formulated on the assumption of surface complex reactions between C–S–H silanol sites and Cs and Sr. The reaction equations and equilibrium constants log $K$ were introduced into PHREEQC by implementing a C–S–H dissolution and precipitation equilibrium model. Here, log $K$ was set on the basis of the least squares method so that the amounts of Cs and Sr adsorbed by C–S–H calculated using PHREEQC fit experimental results.

2. The constructed model that reproduces Cs and Sr adsorption by C–S–H was incorporated into a model that calculates the phase composition of cement pastes based on the thermodynamic phase equilibrium to construct a model that reproduces Cs and Sr adsorption behavior for cementitious materials. To verify the constructed model, the authors attempted to reproduce the results of experiments conducted on the Cs and Sr adsorption behavior on cement paste samples washed with an aqueous solution of calcium to elute Na and K as well as the Cs and Sr adsorption behavior after carbonation or leaching of the cement paste samples. The results indicate that the model reproduces the Cs and Sr adsorption behavior on cement paste even when Na and K coexist in the aqueous solution of Cs and under external environmental actions such as carbonation or leaching. Accordingly, the model constructed in this study was considered to be valid for F1NPS decommissioning plans as an elemental technique using numerical calculations to predict the adsorption of Cs and Sr in contaminated concrete that has been subjected to various external environmental actions.

3. To bring predictions of Cs and Sr migration in contaminated concrete at F1NPS closer to the actual phenomena, the following issues must be addressed in future: modeling of structural changes in C–S–H due to external environmental actions, adsorption of ions by the resulting alumina silica gel generated by carbonation, and adsorption by carbonates and hydrates other than C–S–H especially for Sr, as well as incorporation of these into this study’s model to calculate the phase composition of cement pastes.

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