

**The Influence of Calcium Ions on Migration of Colloidal Silicic Acid in the Presence of Solid Phase  
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**ABSTRACT**

Cementitious materials for the construction of the radioactive waste disposal system could significantly alter the pH (from 8 to 13) of groundwater and release the alkaline components like calcium (Ca) ions. Under such conditions, it is important in the performance assessment of the repository to consider the dynamic behavior of silicic acid. While high pH condition dissolves silicate minerals, the soluble silicic acid deposits or precipitates on solid phase with the decrease of pH by mixing alkaline groundwater with the surrounding groundwater (pH=8). Such alteration processes might lead to clogging of flow-paths around the repository. On the other hand, the flow-path surface would seriously degrade the sorption properties of radionuclides once the flow-path surface is covered with the amorphous silica due to the deposition of colloidal silicic acid. Furthermore, the presence of other ions would complicate such dynamic behavior of the silicic acid. This study focused on the migration of colloidal silicic acid, estimating the migration range depending on the concentration of Ca ions by using one-dimensional advection-dispersion model to consider the deposition rate based on the authors' previous study. The mathematical model applied a first-order reaction to the deposition rate of colloidal silicic acid in the presence of solid phase. Here, the apparent rate constants were described by a function of Ca ions concentration and the specific surface area in an isothermal condition. In the results, the concentration of Ca ions has a strong influence on the spatial deposition range. That is, the colloidal silicic acid can migrate over the range of 100 m around the repository. Besides, the migration range of colloidal silicic acid changes widely, even if the Ca concentration is limited in the range from 0.1 mM to 1.0 mM. These suggest that the presence of Ca ions and the slight difference in Ca concentration have the potential to significantly affect the migration of radionuclides in the natural barrier of the geological disposal system.

**INTRODUCTION**

The dynamic behavior of silicic acid is one of the critical factors for the performance assessment of the radioactive waste disposal system after the backfill. Silicic acid around the repository undergoes dissolution, deposition, precipitation and polymerization depending on the change of pH and temperature. Particularly, since cementitious materials for the construction of repository greatly alter the pH (from 8 to 13) of groundwater and release the cementitious components such as calcium (Ca) ions [1], the dynamic behavior of silicic acid must be taken into account. The solubility of silicic acid markedly increases with

pH>9 [2]. For example, the change of pH from 8 to 13 leads to the dissolution of silicate minerals, and, in contrast, the change of pH from 13 to 8 causes the deposition and polymerization of silicic acid because of a supersaturated condition of silicic acid. Some of such behavior of silicic acid may facilitate the migration of radionuclides from the repository. That is, the deposition and precipitation of silicic acid could alter the chemical properties of flow-paths surface, and affect the adsorption of radionuclides. Then, the colloidal species accelerate the migration of radionuclides because of the complex formation between the colloidal species and radionuclides [3]. On the other hand, the deposition and precipitation of silicic acid may retard the migration of radionuclides, due to the clogging-effect in main flow-paths and in the micro-cracks of rocks [4]. Furthermore, these behavior of silicic acid are affected by the coexisting ions in groundwater. Especially, the concentration of Ca ions around the repository becomes higher compared to that in general groundwater due to leaching from cementitious materials.

The authors have previously examined the dynamic behavior of colloidal silicic acid in the presence of solid phase at neutral pH ( $\approx 8$ ). Chida et al. [5] reported the deposition rates of colloidal silicic acid depended on the surface area of solid phase. In addition, Chida et al. [6] discussed the influence of Ca ions on the dynamic behavior of colloidal silicic acid in the presence of solid phase. However, in these previous studies, the authors did not estimate the spatial range altered by the supersaturated silicic acid, i.e., the migration range of colloidal silicic acid. In this study, firstly, the deposition rates of colloidal silicic acid were summarized on the basis of the authors' previous studies. Next, applying the deposition rates to the advection-dispersion model, the spatial range of the altered area and the migration of colloidal silicic acid were estimated in order to discuss the influence of Ca ions on the migration of colloidal silicic acid in the presence of solid phase.

## **AUTHORS' PREVIOUS STUDIES**

So far, the authors have examined the deposition rate of colloidal silicic acid [5, 6]. The experimental procedure and the results are as follows: The silicic acid solution was prepared by dissolving water glass ( $\text{Na}_2\text{SiO}_3$  solution obtained from Wako Pure Chemical Industries, Ltd.) in distilled ultrapure water. The initial concentration of soluble silicic acid was set to  $1.4 \times 10^{-2}$  M (pH>10). This silicic acid solution was put into the polyethylene vessel with cover (solution volume, 250 ml), and mechanically stirred with a polypropylene stirrer. The temperature was kept constant within  $298 \pm 0.5$  K by the water bath. To avoid contact with air and absorbing carbon dioxide, nitrogen was passed through the vessel. As a solid phase, these studies used pure amorphous silica (Mallinckrodt Co.) in a size fraction of 74-149  $\mu\text{m}$ . Its specific surface area (BET  $\text{N}_2$  gas) was  $322 \text{ m}^2/\text{g}$ . A weighted amount of amorphous silica (0.5 g, 0.3 g, 0.1 g) was poured into the vessel. Then, the pH of the solution was set to 8 with an  $\text{HNO}_3$  solution and a buffer solution mixing MES (2-(*N*-morpholin) ethanesulfonic acid) and THAM (tris(hydroxymethyl) aminomethane). For the condition coexisting Ca ions, promptly after adjusting of pH, a  $\text{Ca}(\text{NO}_3)_2$  solution was added into the solution. The concentration of silicic acid was determined by the silicomolybdenum- yellow method [7] and inductively coupled plasma atomic emission spectrometry (ICP-AES), after aliquots had been filtered through the disposable  $0.45 \mu\text{m}$  membrane filter. In these studies, soluble silicic acid (monomeric or oligomeric silicic acid) was defined as silicic acid reacting molybdate reagent and coloring yellow, and colloidal silicic acid was defined as silicic acid in liquid

phase except for soluble silicic acid [8]. Its total concentration of silicic acid in liquid phase was measured by ICP-AES. Thus, the concentration of colloidal silicic acid was determined as the total concentration of silicic acid in liquid phase minus the concentration of soluble silicic acid. As well, the concentration of the deposited silicic acid was defined as the initial concentration of soluble silicic acid minus the total concentration of silicic acid in liquid phase.

Fig.1 shows the examples of change in the fractional contributions of colloidal silicic acid (the solid lines are discussed later). The fractional contribution,  $f$ , is defined as the amount fraction of colloidal silicic acid to the initial amount of soluble silicic acid. Here, the decrease in the fraction of colloidal silicic acid means the increase in the fraction of deposited silicic acid. As shown in Fig. 1(a), the deposition rate of the colloidal silicic acid specifically depended on the amount of amorphous silica (= the surface area of solid phase). In Fig. 1(b), the deposition rates of colloidal silicic acid in the presence of Ca ions were lower than that under the Ca-free condition. In other words, colloidal silicic acid with Ca ions in liquid phase would be more stable than that in Ca-free solution. (On the other hand, when the concentration of Ca ions exceeded 10 mM (not shown), it was confirmed that Ca ions accelerated the aggregation and precipitation of the colloidal silicic acid.) On the other hand, the fraction of soluble silicic acid decreases immediately after the experiment starts, and becomes almost constant. In this metastable state, the concentration of soluble silicic acid was slightly higher than its solubility at pH 8, i.e., 2.0 mM. After the soluble silicic acid reaches the metastable state, the decrease in the amount of colloidal silicic acid means the deposition amount of silicic acid on the solid phase.

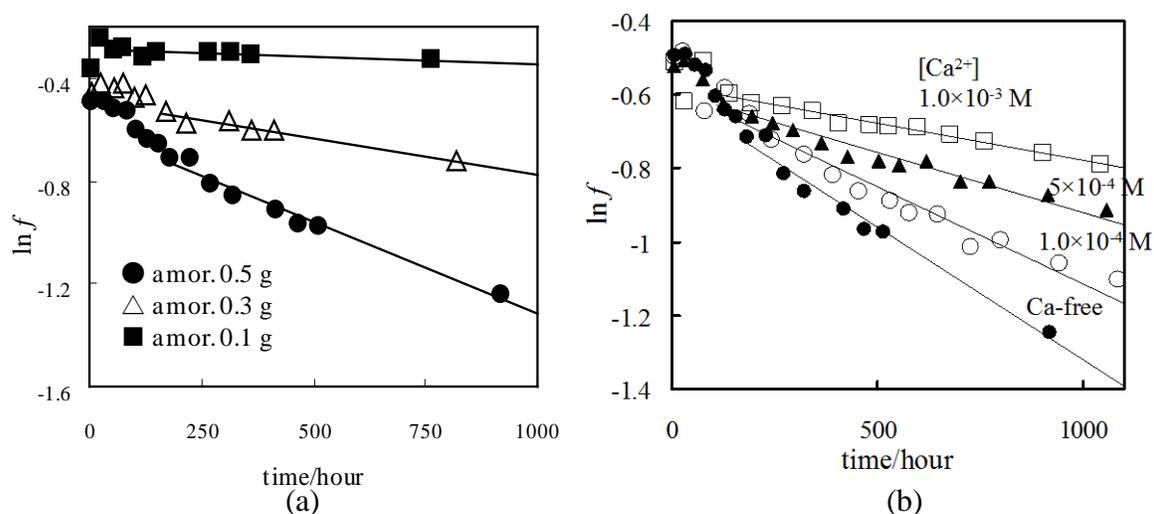


Fig. 1. Fractional contribution of colloidal silicic-acid.

(a) The amorphous silica (0.5 g, 0.3 g, 0.1 g) under Ca-free condition [5].

(b) The amorphous silica 0.5 g and Ca concentration (●: Ca-free, ○: 0.1 mM, ▲: 0.5 mM, □: 1.0 mM) [6].

This study applied the following first-order reaction equation to the decrease of colloidal silicic acid as shown in Fig.1:

$$\frac{df_c}{dt} = -k_c f_c \quad , \quad (1)$$

where  $f_c$  is the colloidal silicic acid fraction,  $t$  is the time (s), and  $k_c$  is the apparent rate constant (1/s). Eq. (1) yields

$$\ln f_c = -k_c t \quad . \quad (2)$$

In Fig. 1, the solid lines are the results of fitting Eq. (2) to the fraction of colloidal silicic acid. The data at  $dC_s/dt > -0.002$  were used for the fitting, where  $C_s$  is the concentration of soluble silicic acid. From the slope of each line, the apparent rate constant,  $k_c$ , was obtained, and  $k_c = ak_0$ , where  $a$  is the surface area per unit volume for the solid phase (1/m) and  $k_0$  is the rate constant (m/s). Applying the rate constant  $k_0$  to the advection-dispersion model, this study estimated and discussed the range of the altered area and the migration of colloidal silicic acid.

## MATHEMATICAL MODEL

### Advection-Dispersion Model

Fig. 2 shows an illustration of the mass balance, considering the advection, the dispersion and the interaction of radionuclide with the solid phase. In a conservative sense, this study focused on the altered spatial range from the repository, by ignoring the clogging-effect of the colloidal silicic acid. That is, it is assumed that the change of fluid flow velocity due to the deposition is negligible small. In such a case, the solute migrates due to the advection and dispersion with repeating the adsorption and desorption on the solid surface. Based on Fig. 2, the one-dimensional mass balance can be described by

$$\Delta t A (q_x - q_{x+\Delta x}) + \Delta t A \{ (uc)_x - (uc)_{x+\Delta x} \} - \Delta x A \varepsilon c a k^+ \Delta t + (1 - \varepsilon) \Delta x A s a k^- \Delta t = \Delta x A \varepsilon (c_{t+\Delta t} - c_t) \quad (3)$$

where  $c$  is the concentration of the solute in liquid phase (mol/m<sup>3</sup>),  $\varepsilon$  is the porosity of the porous medium (-),  $u$  is the flow velocity (m/s),  $t$  is the time (s),  $\Delta t$  is the infinitesimal time step/increment (s),  $x$  is the distance (m),  $\Delta x$  is the infinitesimal distance change,  $q$  is the flux (kg/m<sup>2</sup>s),  $s$  is the solute concentration in solid phase (mol/m<sup>3</sup>),  $k^+$  is the rate constant for the adsorption (1/s),  $k^-$  is the rate constant for the desorption (1/s),  $A$  is the cross section of flow pass (m<sup>2</sup>), and  $a$  is the specific surface area (1/m). As Eq. (3) is rewritten as a differential equation, we obtain

$$D_e \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} - a k^+ c + a k^- s = \varepsilon \frac{\partial c}{\partial t} \quad (4)$$

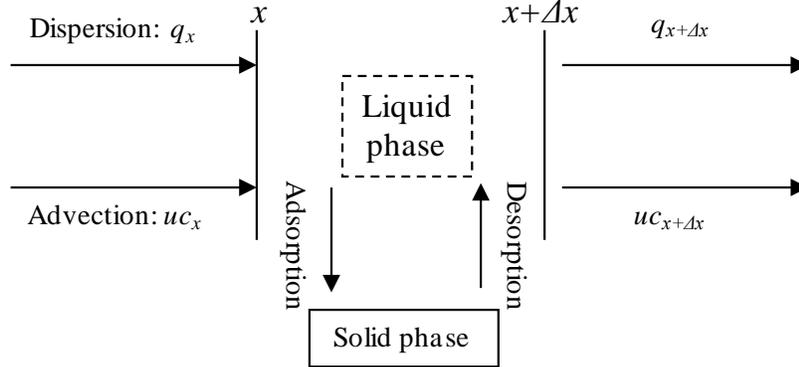


Fig. 2. Illustration of the one-dimensional mass balance.

where  $k^+ = \varepsilon k^+$ ,  $k^- = (1-\varepsilon) k^-$ ,  $q = -D_e(\partial c/\partial x)$  (defined by Fick's law), and  $D_e$  is the effective dispersion coefficient ( $\text{m}^2/\text{s}$ ). For the migration of colloidal silicic acid, the desorption rate is assumed to be negligibly small (i.e., the sorption reaction is irreversible) with a supersaturated condition of silicic acid in groundwater ( $\text{pH} \approx 8$ ), and Eq. (4) is simplified to

$$D_e \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} - kc = \varepsilon \frac{\partial c}{\partial t} \quad , \quad (5)$$

where  $k$  is the rate constant including the specific surface area ( $1/\text{s}$ ). The dimensionless form of Eq. (5) is

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} - D_a C = \frac{\partial C}{\partial T} \quad , \quad (6)$$

where  $C = c/c^*$ ,  $X = x/x_1$ ,  $T = t/t^*$ ,  $t^* = \varepsilon x_1/u$ ,  $P_e = ux_1/D_e$ , and  $D_a = kx_1/u$ ;  $c^*$  is the input concentration of the solute in  $0 \leq t \leq t_{in}$  ( $\text{mol}/\text{m}^3$ ),  $x_1$  is the characteristic length (length of flow-path) (m),  $t^*$  is the characteristic time (s),  $P_e$  is the Peclet number (-) ( $= 10$  [9]),  $D_a$  is the Damköhler number (-). The initial condition is  $T = 0$ ,  $C = 0$ . The input conditions of the solute are  $0 \leq T \leq T_{in}$ :  $C_{X=0-} = 1.0$ ,  $T_{in} < T$ :  $C_{X=0-} = 0$ , where  $T_{in}$  is the input time (-). The value of  $T_{in}$  should be smaller than 0.05 of the characteristic time to get an impulse response [10]. The boundary conditions are

$$C_{X=0-} = C_{X=0+} - \frac{1}{P_e} \frac{\partial C}{\partial X} \Big|_{X=0+} \quad , \quad X = 1 : \partial C/\partial X = 0 \quad , \quad (7)$$

where Eq. (7) is the closed vessel boundary condition [10]. This study used the FTCS (forward time central space) finite difference method for solving Eq. (6). In discretizing the advection terms in Eq. (6), the first-order upwind difference method was used.

**Arrangement of Rate Constants**

In this study, the deposition rate-constants of colloidal silicic acid are reflected on the Damköhler number,  $D_a$ . Fig. 3 shows the assumed one-dimensional parallel flat board (as a simplified form of fracture). The surface area per unit volume in Fig. 3,  $a_f$ , is defined by  $2/\delta$  ( $= 2\Delta x l / \Delta x l \delta$ ). For example, when  $\delta = 0.1$  mm [11], the surface area  $a_f$  becomes  $2 \times 10^4$  1/m. The rate constant in  $D_a$  is defined as  $k = a_f k_0$ . As stated above, the values of  $k_0$  are determined by the previous experimental results. Assuming  $u = 3.17 \times 10^{-8}$  m/s [11] and setting  $x_l$  in the range of 10 to 100 m, the values of  $D_a$  were estimated by using the deposition rate-constants,  $k_0$ , as shown in Table I.

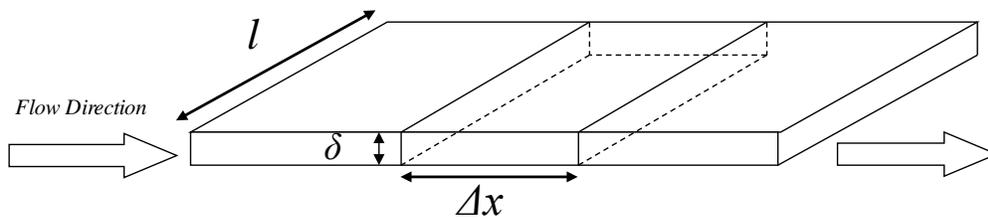


Fig. 3. The one-dimensional parallel flat board.

Table I.  $D_a$  estimated from the deposition rate-constants under each experimental conditions.

	Experimental conditions	$k_0$ [m/s]	$D_a$ ( $x_l=10$ )	$D_a$ ( $x_l=20$ )	$D_a$ ( $x_l=50$ )	$D_a$ ( $x_l=100$ )
Case 1	Ca-free Amorphous silica 0.1g	$8.75 \times 10^{-14}$	0.55	1.10	2.76	5.52
Case 2	Ca-free Amorphous silica 0.3g	$1.60 \times 10^{-13}$	1.01	2.02	5.05	10.1
Case 3	Ca-free Amorphous silica 0.5g	$2.60 \times 10^{-13}$	1.64	3.28	8.20	16.4
Case 4	Ca 1.0 mM Amorphous silica 0.5g	$6.95 \times 10^{-14}$	0.44	0.88	2.19	4.38
Case 5	Ca 0.5 mM Amorphous silica 0.5g	$1.15 \times 10^{-13}$	0.73	1.45	3.63	7.26
Case 6	Ca 0.1 mM Amorphous silica 0.5g	$1.84 \times 10^{-13}$	1.16	2.32	5.80	11.6

**RESULTS AND DISCUSSION**

Fig. 4 shows the normalized concentrations of colloidal silicic acid calculated by using Eq. (6) at  $x_1 = 50$  m. Here, the horizontal axis is the normalized time. The rate constants  $k$  depending on both the surface area and the Ca concentration in the experiments reflect the retention time of colloidal silicic acid. For example, Case 1 undergoes the relatively high concentration of the colloidal silicic acid at the point of 50 m from the feed point of the colloidal silicic acid, i.e., the location of the repository. This means that the deposition of colloidal silicic acid is not enough on the surface of flow path in the range from 0 to 50 m. In other words, the colloidal silicic acid alter the surface of flow path further downstream from the point of 50 m. Such a tendency appears more remarkably in the presence of Ca ions as coexisting ions, as shown in Figs.4 (a) and (b), when its concentration of Ca ions is limited in the range up to 1.0 mM. (As mentioned above, when the concentration of Ca ions exceeded 10 mM, Ca ions accelerated the aggregation and precipitation of the colloidal silicic acid.) On the other hand, Case 3 in Fig. 4 shows that most of colloidal silicic acid deposited on the surface of flow path within the range up to 50 m. Therefore, the alteration due to the deposition is limited in the range further downstream from the point of 50 m.

Fig. 5 shows the dependencies of the colloidal silicic acid concentration on the characteristic length  $x_1$  (= the distance of flow path), by using the examples of Case 4. The peak of normalized concentration of colloidal silicic acid became small as  $x_1$  became large from 10 m to 100 m. However, part of colloidal silicic acid can reach the range of 100 m. For the comparison of each condition, in Fig. 6, the peak values

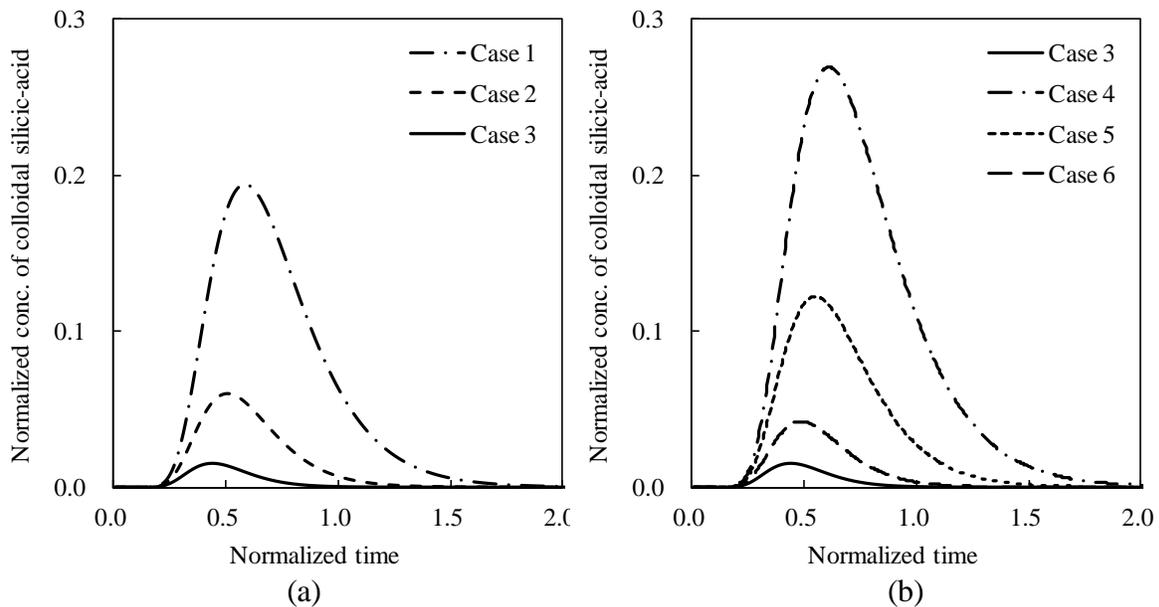


Fig. 4. Calculation examples of the normalized concentrations of colloidal silicic acid at  $x_1=50$  m. (a) Cases 1-3, (b) Cases 3-6

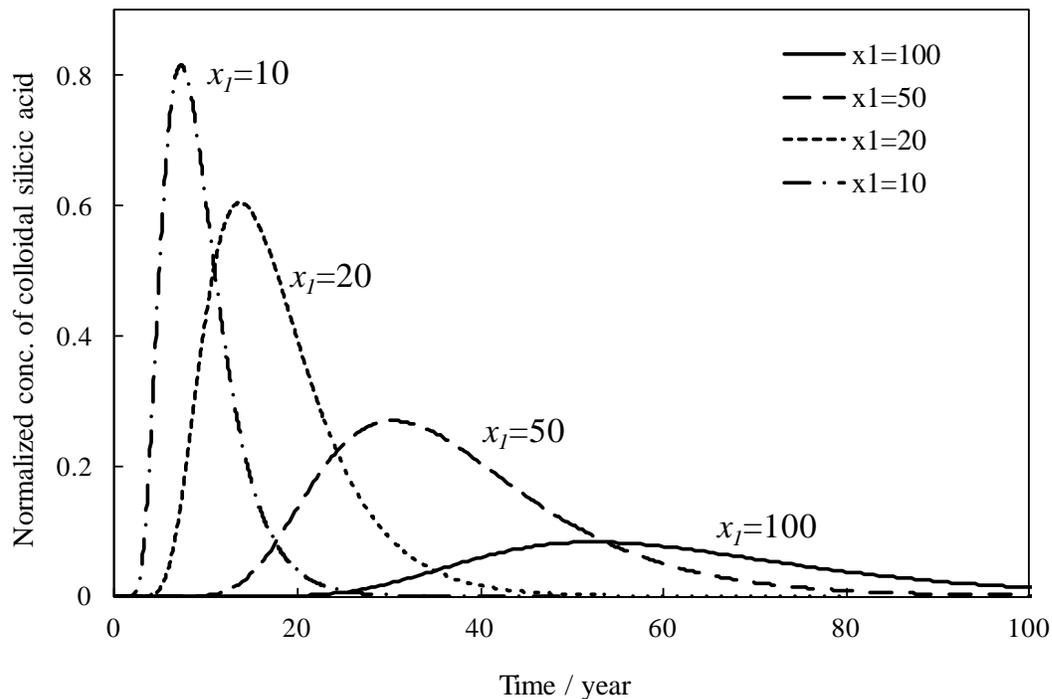


Fig. 5. Dependencies of the concentration of colloidal silicic acid on the characteristic length  $x_l$  (Case 4).

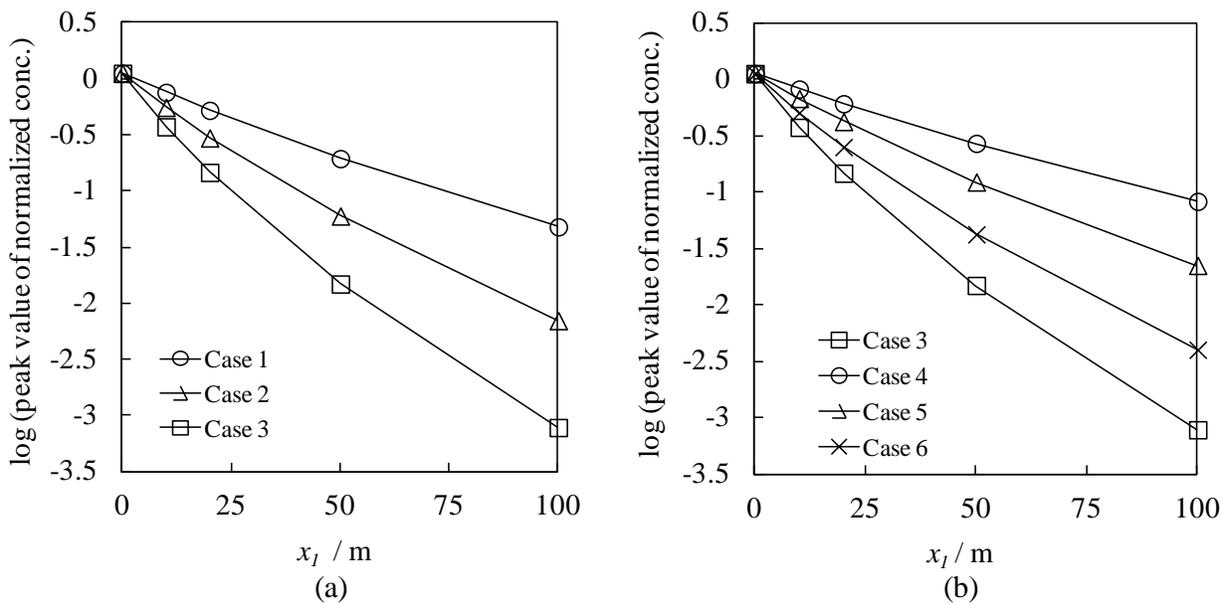


Fig. 6. The normalized concentrations at the peak to the characteristic length (the distance of flow path)  $x_l$ . ((a) Ca-free, Cases 1-3, (b) coexisting Ca ions, Cases 3-6)

of the normalized concentration are indicated. Here, the horizontal axis is the distance of flow path ( $= x_1$ ). These peak heights reflect a potential to migrate the colloidal silicic acid further downstream from a given distance of flow path. As shown in Fig. 6(a), the surface area strongly affects the peak values of the colloidal silicic acid. At the point of 100 m in  $x_1$ , for example, when the surface area of solid phase becomes five times (Note Case 1 and Case 3), the peak values of colloidal silicic acid increases 100 times. Besides, as shown in Fig. 6(b), the deposition of colloidal silicic acid became slower and the migration of colloidal silicic acid could be accelerated as the concentration of Ca ions became higher. At  $x_1 = 100$ , the peak value of colloidal silicic acid in the condition of 1.0 mM in Ca ions (Case 4) becomes 100 times larger compared to that in the condition of Ca-free (Case 3). This means that, even if the Ca concentration is limited in the range up to 1.0 mM, the presence of Ca ions and the slight difference in Ca concentration greatly affect the migration of radionuclides in the natural barrier of the geological disposal system.

In this study, the values of the characteristic length  $x_l$  were set in the range of 10 to 100 m, and the results showed the colloidal silicic acid can migrate over the range of 100 m around the repository. Japan Nuclear Cycle Development Institute's (now Japan Atomic Energy Agency's) H12 report assumed 100 m (i.e.,  $x_1=100$ m) as a flow path from the repository to large faults [11]. In such a case, the results in this study suggest that the colloidal silicic acid may reach the faults, altering the flow-path surface of amorphous phase. Once the flow path surface is covered (altered) with the amorphous phase due to the deposition of silicic acid, it would take more than several million years in order to crystallize the surface of the solid phase. Therefore, such an alteration affects the migration of radionuclides released from the repository. As mentioned above, the cementitious materials might form colloidal silicic acid in an alkali front (a mixing zone of high alkaline plume with natural groundwater (pH $\approx$ 8)). Niibori et al. [12] also reported that the alteration of the solid surface with colloidal silicic acid degrades the adsorption property for radionuclides. However, since cement is an essential material for the construction of the repository located below water table, it would be useful to also examine the change of fluid flow velocity caused by the clogging-effect of the deposition reactions, using more reliable models that consider other depositions of secondary minerals such as calcium-silicate-hydrate in the presence of Ca ions. Additionally, for understanding the migration dynamics of colloidal silicic acid, it is also necessary to consider the colloidal form, the coexisting ions (electrolytes), the solid phase. In the future, it is expected that migration models are continuously improved by reflecting experimental results about each factor.

## **CONCLUSIONS**

This study estimated the potential migration range of colloidal silicic acid depending on the concentration of Ca ions by using one-dimensional advection-dispersion model that consider the deposition rate under a supersaturated condition of silicic acid based on the previous works. In the calculation results, the presence of Ca ions ( $\sim$ 1.0 mM) accelerated the migration of colloidal silicic acid compared with the condition of Ca-free, and even in the limited range of Ca concentration up to 1.0 mM, the migration of colloidal silicic acid was significantly affected. Generally, the concentration of Ca ions does not exceed 10 mM even if the groundwater is altered by cementitious materials. Therefore, in the performance assessment of the geological disposal system, the relation of colloidal silicic acid and Ca ions is an

important factor. In order to examine the clogging-effect of the deposition reactions on the migration of radionuclides, we would need more reliable models to consider other depositions of secondary minerals such as calcium-silicate-hydrate in the presence of Ca ions.

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